Journal of CHEMICAL EDUCATION

VOLUME 23 — *May, 1946* — NUMBER 5

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Subscription Price: Domestic $3.00 per year; Countries in Pan-American Union $3.00 per year; Canada $3.50; other countries $4.00. Issued monthly. Single copies of issues in current year, 50c each; all other single copies, one dollar. Foreign remittances must be accompanied by International Money Order.

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Entered as second-class matter, January 31, 1924, at the Post Office at Easton, Pa., under the act of March 3, 1879. Accepted for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized January 31, 1924.

The JOURNAL OF CHEMICAL EDUCATION *is the official organ of the Divisions of Chemical Education and History of Chemistry and incorporates the Report of the New England Association of Chemistry Teachers. It is indexed in the Education Index, Industrial Arts Index, and, in part, in the Quarterly Cumulative Index Medicus*

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Portrait of Madame Lavoisier (*see page 210*)

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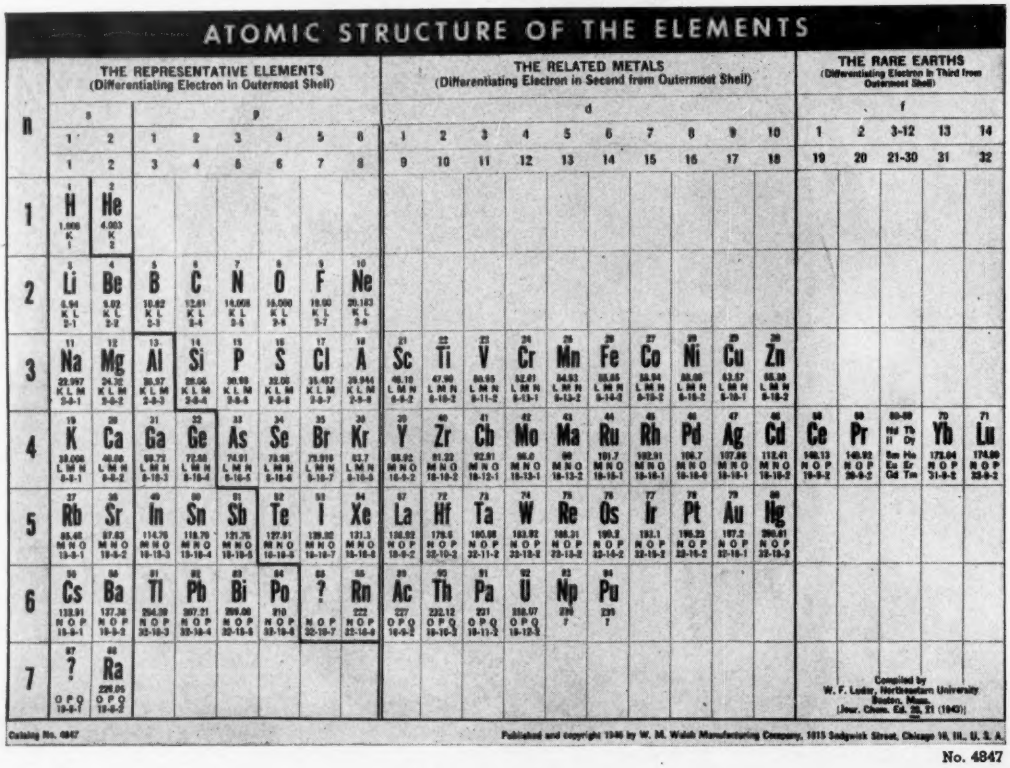
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Editor's Outlook

HE WAS fresh out of the service, and he hadn't been in very long, judging from his age. "Oh, yeah?" he said to the drugstore clerk, a friend of his. "Well, all this stuff about the G. I. Bill of Rights and sending veterans to college is nothing but a bunch of malarkey. 'Cause you've still got to have the grades in high school, just like you always did."

Disillusionment. Somehow it had seemed that the agony of war should have brought about a short-cut to knowledge and wisdom. Congress could have set it up that way if it had wanted to, but instead it just let the guys down. Guess we don't have the right men down there in Washington.

Or maybe we don't—or up there in the State Capitol. That remains to be seen, because sooner or later the too-broad application of the principle, "what's good enough for one is good enough for all," may lead to political tampering with the educational machinery. We didn't make much distinction when we pulled them out of school and sent them off to war, so why should we do so when we put them back in again?

They say that 4,000,000 may take advantage of the veterans' educational benefits, and that's worth a cheer. For it has always been our national policy and belief that the more of our people who can absorb more education, the more hope there is for the future of the country. But there are long-range as well as short-range aspects of the problem, and we must not let an academic "housing shortage" put permanent dents in our higher educational equipment.

Expand in the middle, organize temporary schools if necessary, but don't overload the delicate machinery so as to prevent production at the level of scholarship and research.

The crowding of our colleges and universities during the next few years will make it difficult if not impossible to take in a normal quota of foreign students. This is unfortunate, not because we owe anything to foreign visitors, but because this is particularly the time when cordial foreign relations should be most strenuously cultivated and the education of foreign students has been one of the most effective means of doing so. A few hundred Russian students in our institutions would do more to promote understanding between our two countries than a dozen formal diplomatic meetings.

It is expected that, by and large, priority for entrance to college will be given veterans and no serious fault can be found with that policy, of course. It looks as though "civilian" boys fresh from high school will find the pickings pretty slim for a while. Is this the beginning of another "lost generation"?

President Morrill of the University of Minnesota said recently, "The veterans' crisis is a crisis in American democracy. It is a test of our faith in education as the surest safeguard not only of individual opportunity but of democracy."

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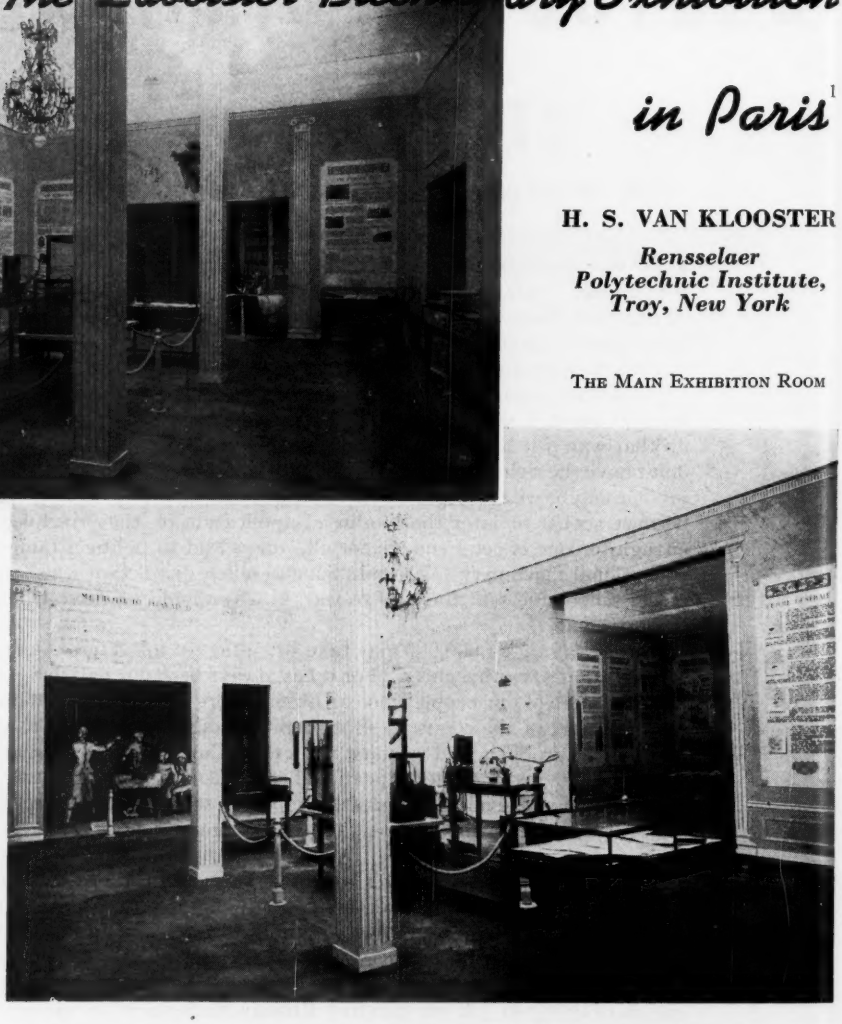
The Lavoisier Bicentenary Exhibition in Paris[1]

H. S. VAN KLOOSTER

Rensselaer Polytechnic Institute, Troy, New York

THE MAIN EXHIBITION ROOM



ALTHOUGH the bicentenary of the birth of Lavoisier has not gone unnoticed in the world literature of chemistry, very little is known outside France of the commemoration of this event in the city of Paris where the patron saint of French chemistry was born, worked, and found an untimely death on the guillotine on May 8, 1794. This lack of knowledge was probably due to the news blackout maintained by the Germans. It is refreshing to find that in spite of innumerable difficulties, M. Gabriel Bertrand of the *Institut Pasteur*, president of the French Academy of Sciences, was able to organize a Lavoisier exhibition in the *Palais de la Découverte*.[2] The exposition, which was quite successful, lasted from November, 1943, to January, 1944. The preliminary work was begun early in 1943 and resulted in uncovering a multitude of documents, books, personal mementos, instruments, glassware, and collections (mineralogic, geologic, and botanic).[3] These give an impressive idea of the many-sided activities undertaken by the father of modern chemistry during the relatively short period of 30 years.

Lavoisier was the son of well-to-do parents, his father being attorney (*procureur*) to the *Parlement* of Paris. On leaving the *Collège Mazarin*, he studied to become a lawyer and was admitted to the profession in 1764 at the age of 21; however, having acquired a liking for science, he deserted the law and turned to mathematics, astronomy, botany, geology, anatomy, meteorology, and chemistry. It seems that the geologist, Guettard, a friend of the family who took young Lavoisier repeatedly on geological excursions, exerted a powerful influence in converting him to a scientific career. Next to Guettard, it was Rouelle, demonstrator at the *Jardin des Plantes*, who aroused Lavoisier's interest in chemistry. As a matter of fact, his first publication in 1765 dealt with the setting of

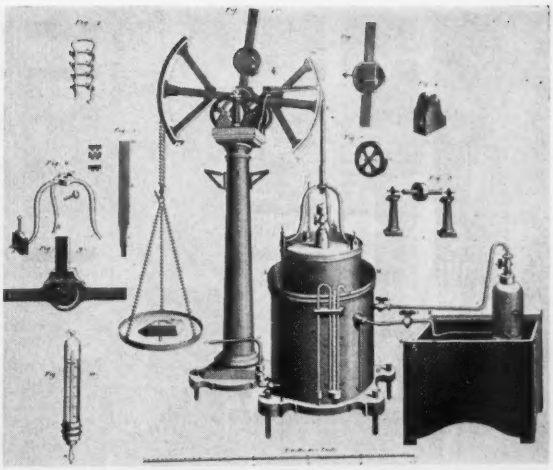
[1] Presented before the Division of Chemical Education at the 109th meeting of the American Chemical Society in Atlantic City, April 8–12, 1946.

[2] This museum of natural sciences, the building of which was due to the initiative of the late Jean Perrin, forms an addition to the *Grand Palais*. It has a separate entrance on the *Avenue Franklin D. Roosevelt*, formerly *Avenue Victor Emanuel II*. It was opened in 1937.

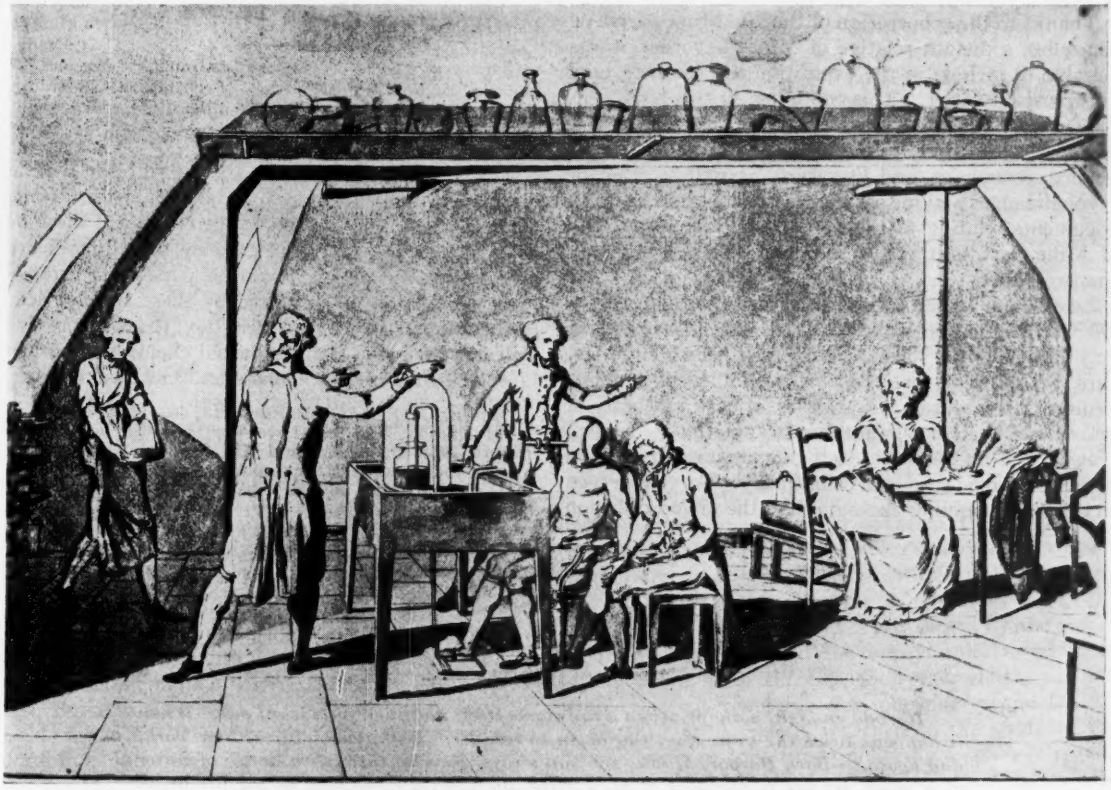
[3] The permanent repository of Lavoisier's instruments is the museum of the *Conservatoire National des Arts et Métiers* in the *Rue St. Martin*.

plaster of Paris. The following year he received a gold medal from Louis XV as a reward for his essay on the best means of providing street illumination in large cities. This was the starting point for his long-continued studies of combustible materials and combustion in general, which culminated in the overthrow of the phlogiston theory around 1790.

Admitted at the age of 25 to the *Académie des Sciences*, he joined at the same time (March, 1768) the *Fermiers Généraux*, a group of administrators to whom the collection of taxes was farmed out by the State. While this assured him an ample income with which to carry out his researches, it was this association which later led him to the guillotine. Through his colleague at the *Ferme*, Jacques Paulze, he came to know the latter's daughter, Marie, whom he married in 1771 when he was 28 and his bride barely 14. Appointed administrator of the *Régie des Poudres* in 1775, he lived from then on at the Arsenal where he installed his laboratory. In spite of his many other interests Lavoisier devoted six hours each day, from 6 to 9 in the morning and from 7 to 10 at night, to his scientific studies and, moreover, reserved one day a week entirely for experiments. In this work he was ably seconded by his wife and a group of enthusiastic coworkers. A sketch of Lavoisier's laboratory from the hand of Mme. Lavoisier, who was a gifted artist, a competent translator, and an able private secretary, served as a basis for the reconstruction of his laboratory for the Paris exhibition. The skillful drawing of her husband's apparatus for organic combustions enabled the staff of the *Palais de la Découverte* to rebuild this piece of



A SKETCH OF SOME OF LAVOISIER'S APPARATUS, DRAWN BY MME. LAVOISIER. (THE ORIGINALS MAY BE SEEN IN THE ILLUSTRATIONS OF THE MAIN EXHIBITION ROOM)



A RECONSTRUCTION OF LAVOISIER'S LABORATORY, DRAWN BY MME. LAVOISIER

A RECONSTRUCTION OF LAVOISIER'S STUDY

equipment so faithfully that it could be used at once by its originator were he to resume his researches after the lapse of a century and a half.

Thanks to the cooperation of the late Mme. Pierre de Chazelles, a distant relative of Mme. Lavoisier, it was possible to include in the exposition the reconstructed library of Lavoisier. This contained in two bookcases the volumes he earned as prizes at the *Collège Mazarin*, his own works, sundry volumes on science, history, finance, economics, and literature, as well as a set of royal almanacs and miscellaneous papers, registers, and documents relating to the *Ferme Générale*. A picture of Mme. Lavoisier can be seen on the wall between the two bookcases.

Last August when the writer visited the *Palais de la Découverte*, a considerable part of the Lavoisier exhibit was on display in various glass cases. Two large lecture tables were reserved for a number of familiar demonstrations, such as analysis of air, synthesis of water, combustion of phosphorus and iron in oxygen, transition from the liquid to the vapor state, formation of carbon dioxide, and ice calorimetry. As can be seen in the accompanying photograph of the main exhibition room, a number of instructive, decorative, and descriptive tables and charts provide the visitor with a bird's-eye view of Lavoisier's versatile accomplishments.

A brochure of 55 pages, profusely illustrated, gives complete details of the exhibition and contains, furthermore, a little-known article on Lavoisier by Pasteur, reprinted from the September issue of the *Moniteur Universel* of 1869. This article gives Pasteur's estimate of the three men whose names are for all time associated with the story of oxygen.

There is no need to go into this controversial matter here. It has been discussed elsewhere.[4,5] Suffice it to repeat what Professor Donnan wrote in the introduction to McKie's book (p. 8):

> I will never forget the feelings of admiration for the power of the human mind and spirit, which I experienced, when I first read Lavoisier's great "*Traité Élémentaire de Chimie.*" It should be read by every student of science and learning, for it is one of the immortal landmarks in the history of civilization. Will not the *Institut de France* issue a cheap facsimile edition, which could be placed in the hands of every young student?

Thanks are hereby expressed to Professor Bertrand for a reprint of his address published in the *Mémoirs* of the *Institut* for 1943 and to the curator of the *Palais de la Découverte*, M. André Léveillé, who furnished the pictures for this article. Were it possible to arrange a Lavoisier exhibit as organized by these two gentlemen in the adopted country of Priestley, it might provide a welcome diversion from the usual chemical expositions familiar to American chemists and chemical engineers.

[4] OESPER, R. E., J. CHEM. EDUC., **13**, 403–12 (1936).

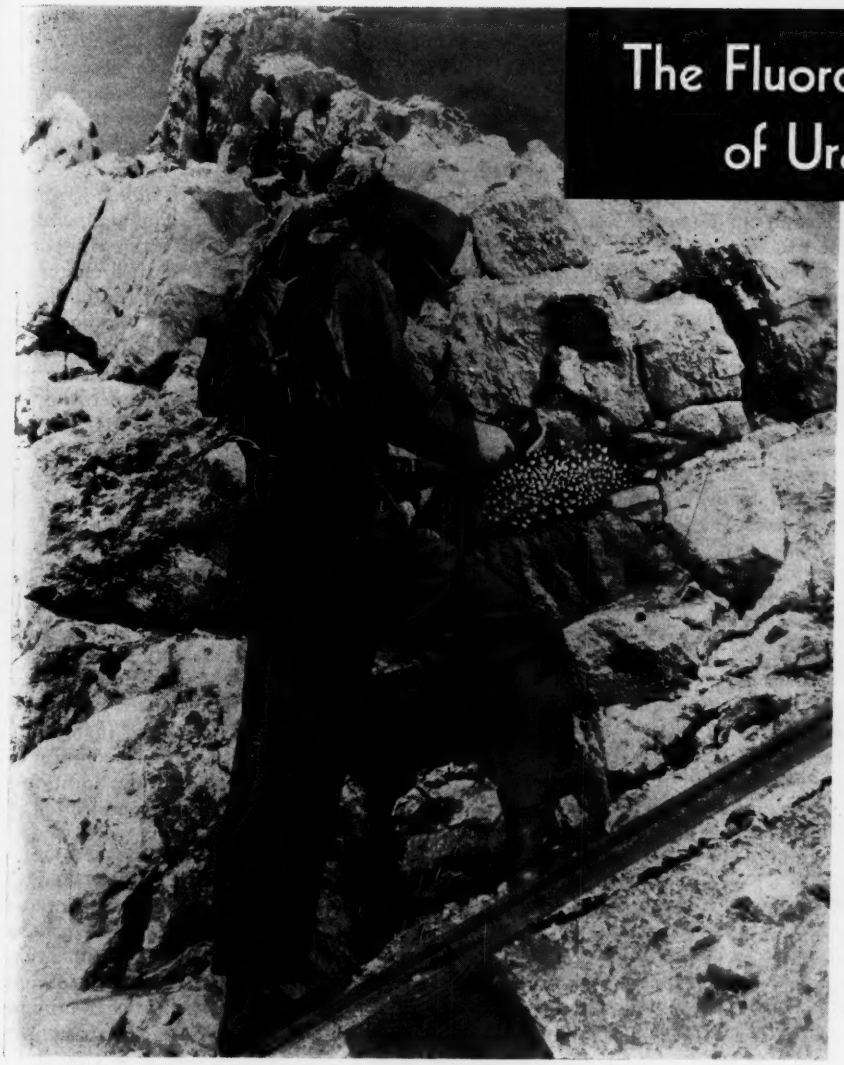
[5] MCKIE, D., "Antoine Lavoisier," J. B. Lippincott, Philadelphia, **1936**, chapters V and VI. See also: FRENCH, S. J., "Torch and Crucible," Princeton University Press, Princeton, **1941**, which contains some new material on the relation between Lavoisier and the du Pont family.

ACCIDENT!

It's odd enough, perhaps, when a fire starts itself and then puts itself out. When it happens twice the same way, you begin to wonder. But once in Utica, New York, and again in Dark Harbor, Maine, the sun's rays, passing through a bottle of water in a truck, set fire to the floor of each truck, only to have the heat of the fire break the bottle and the water put out the flames.

The Fluorochemistry of Uranium

JACK De MENT
Fluorescence Laboratories, Portland, Oregon



THE PORTABLE ULTRAVIOLET LAMP IS NOW BEING TAKEN INTO THE FIELD IN THE SEARCH FOR URANIUM-BEARING MINERALS

FOR almost a century uranium has been associated with great advances in chemistry and physics. Much of our understanding of luminescence has arisen in studies on the uranyl compounds. It was a compound of uranium in which radioactivity was first discovered. And today we owe our successful application of the mass-energy equivalence principle, in the form of atomic bombs, to an understanding of this element.

Nichols and Howes (*1*) in their classic monograph entitled the "Fluorescence of the Uranyl Salts" tell that the beginnings of precise knowledge concerning the luminescence of the uranium compounds are to be found in the memoirs of Sir G. G. Stokes and of Alexandre Edmond Becquerel. It is true that in 1833 Sir David Brewster, who observed the fluorescence of chlorophyll and other substances and gave the phenomenon the name of "internal dispersion," mentioned a yellow glass, doubtless the "canary glass" of commerce, which exhibited the same property (*2*); but it remained for Stokes (1853), by means of the beautiful experiments described in his papers on "The Change in the Refrangibility of Light," to elucidate the phenomena and lay the foundation for all subsequent work on fluorescence (*3*).

Stokes, by ingenious methods of transverse dispersion and crossed light filters (*4*), in a way anticipated modern work on the fluorochemistry of the uranyl salts. He wrote:

> The intervals between the absorption bands of green uranite were nearly equal to the intervals between the bright bands of which the derived spectrum (*i. e.*, the fluorescence spectrum) consisted in the case of yellow uranite. After having seen both systems, I could not fail to be impressed with the conviction of a most intimate connection between the causes of the two phenomena, unconnected as at first sight they might appear. The more I examined the compounds of uranium, the more this conviction was strengthened in my mind.

After this remarkable observation the subject lay dormant for some years. Subsequently E. Becquerel found that fluorescence was shown almost exclusively by the oxygenated uranium compounds—*i. e.*, the uranyl or UO_2 salts—and was not shown by the oxides of uranium. He found the uranyl salts to have an afterglow of some three or four thousandths second, employing his revolving disc phosphoroscope (*cf. 1*).

In 1872 E. Becquerel returned to the study of the uranyl salts, at that time publishing a series of papers setting forth sufficient evidence to draw fairly substantial conclusions about their fluorescence spectra.

At about this time (1873) Morton and Bolton published an account of their extended researches on the fluorescence and absorption spectra of the uranyl salts (*5*).

After the turn of the century Nichols and his coworkers took up the study, publishing a classical memoir on the subject in 1919 (*1*). These students of uranium fluorochemistry took advantage of the discovery of Becquerel and Onnes, made in 1909, that the fluorescence of certain uranyl compounds is resolved into groups of narrow, line-like bands when these substances are cooled to the temperature of liquid air (*6*). Since then supercooling has matured into a tool of the greatest significance in determining the radiation characteristics of a substance.

EXCITATION

In general any optical excitant which, in accordance with the first and second laws of fluorescence (*7*), is absorbed by a uranyl compound will cause light emission. This means short visible light wave lengths, ultraviolet light, and other short wave radiations like X-rays and gamma rays. In most of the uranyl compounds the light released as a consequence of the "quantum-capture" process lies in the green and yellow portions of the spectrum, with blue bands evident in some cases. The brilliant yellow-green fluorescence is caused not only by the optical excitants mentioned, but also by a variety of corpuscular radiations, as well as sundry agents. Thus, electrons (cathode rays and beta particles), alpha particles, miscellaneous ions, protons, deuterons, and probably neutrons excite fluorescence in the uranyl salts.

A strong ultraluminescence has not been reported for any of the uranyl compounds, and a number of studies have been made on this phase of uranium fluorochemistry. The same may be said of the existence of a strong infraluminescence in uranium salts. It was once believed that X-rays might cause uranyl salts to emit large amounts of ultraviolet light, but experiment proved this in error (*cf. 7*).

SUPERCOOLING

Only a brief summary can be given here of the effects of supercooling on the fluorescence spectra of uranyl salts. Tabulations of specific uranium compounds have been given elsewhere by Nichols and his coworkers and by the present writer (*1, 8*). In general, however, many striking effects are seen when the temperature of fluorescing uranyl salts is slowly changed from +20°C. to −180°C. These include: (*a*) an increase in intensity of the entire emission spectrum; (*b*) a shift which is more often toward the violet than the red, though both shifts may occur between the above-mentioned temperatures; (*c*) a narrowing or resolution of the bands, and sometimes a resolution to the extent of causing the disappearance of certain bands; (*d*) a slight alteration in frequency intervals; (*e*) the formation of one or more definite hydrates; and (*f*) a change in the form of the bands.

A good example of uranium fluorochemistry lies in uranyl nitrate. This substance fluoresces strongly under ultraviolet light of all wave lengths, as well as under X-rays. Uranyl nitrate triboluminesces, and when shaken in a tube containing neon gas at low pressure, it will cause the neon to luminesce its familiar orange color. Otherwise, the triboluminescence is greenish or, when quite feeble, a greenish white.

Anhydrous uranyl nitrate shows a much stronger fluorescence in ultraviolet light at room temperature than its various hydrates. The anhydrous compound luminesces a brilliant yellow, with a whitish characteristic, in 3650 A.U. ultraviolet light, and the hydrates, especially the hexahydrate, exhibit a strong green tinge (*9*). The various hydrates of uranyl nitrate show differences in band structure, though a normal solution of the salt in water at room temperature exhibits two strong bands at 5323 and 5088 A.U., resolving at 0°C. to four bands, and then to 20 bands lying between 6165 and 4855 A.U. at the temperature of liquid air (*1*). The water solution of uranyl nitrate is better excited by short wave length, *i. e.*, 2537 A.U., radiations than by the long waves, this fact permitting the detection of small amounts of uranium in solution (described subsequently). Uranyl nitrate in ethyl ether solution does not fluoresce, nor do the ether complexes of this compound, according to the studies of the writer (*9*).

The changes in the fluorescence spectrum of the simpler uranyl salts, like the nitrate, produced by dilution include: (*a*) a shift in the entire spectrum; (*b*) a change of frequency interval; (*c*) a decrease in resolution except when the equilibrium is altered by the addition of small amounts of acid; and (*d*) a decrease in intensity (*1, 9*).

FLUORESCENT URANIUM COMPOUNDS

Except when dissolved in a liquid solvent, like acid, or a solid solvent, like glass, the oxides and peroxides of uranium do not fluoresce. Many, but not all, uranyl salts fluoresce in the crystalline state as well as in liquid and solid solutions. Table 1 lists the principal luminescent uranyl compounds which have been studied through the years. Practically all of these emit in the green, yellow, yellow-green, yellow-blue, or similar portions of the visible spectrum.

TABLE 1

REPRESENTATIVE LUMINESCENT URANYL SALTS

Uranyl acetate	Uranyl nitrate (anhydrous)
Uranyl acid sulfate	Uranyl nitrate (dihydrate)
Uranyl ammonium acetate	Uranyl nitrate (trihydrate)
Uranyl ammonium chloride	Uranyl nitrate (hexahydrate)
Uranyl ammonium nitrate	Uranyl oxalate
Uranyl ammonium phosphate	Uranyl phosphate
Uranyl barium acetate	Uranyl potassium acetate
Uranyl calcium acetate	Uranyl potassium chloride
Uranyl calcium phosphate	Uranyl potassium fluoride
Uranyl cesium chloride	Uranyl potassium nitrate
Uranyl chloride	Uranyl potassium sulfate
Uranyl diammonium nitrate	Uranyl rubidium acetate
Uranyl diammonium chloride	Uranyl rubidium chloride
Uranyl dipotassium nitrate	Uranyl rubidium nitrate
Uranyl fluorammonium fluoride	Uranyl rubidium sulfate
Uranyl iodate	Uranyl silver acetate
Uranyl lead acetate	Uranyl sodium acetate
Uranyl lithium acetate	Uranyl sodium phosphate
Uranyl magnesium acetate	Uranyl sulfate
Uranyl manganese acetate	Uranyl zinc acetate

Several hundred uranium compounds have been listed in the literature, many papers describing them dating back almost a century and including such familiar names as J. J. Berzelius. The two most comprehensive summaries of uranium compounds in the English language are those of Mellor (*10*) and De Ment and Dake (*11*), the latter writers including minerals and fluorescent salts.

URANIUM AS AN ACTIVATOR

Trace amounts of uranium in solid solution in a bulk of solid solvent—*i. e.*, the heterogeneous luminescent system or phosphor—are often responsible for the luminescence seen in various minerals and glasses. As an activating agent, uranium is of increasing importance for the production of fluorescent glasses and for the preparation of numerous different crystal phosphors. The uranium-activated crystal phosphors are beyond the scope of the present discussion though extended treatments have been given the subject elsewhere (*7, 11, 12*). The state of uranium in various bases is presently the subject of considerable controversy. For the phosphors synthesized at relatively low temperatures the uranyl radical appears to remain intact. In glasses and high-temperature phosphors this is not true, for an activating action is secured by otherwise nonfluorescent uranium compounds, such as uranium dioxide. The valency of the uranium atom in a phosphor base is also the subject of contention, and anomalous values are often ascribed—*e. g.*, uranium with a valence of one, two, three, and four—in view of our present knowledge (*13*).

The fact that uranium imparts fluorescence to glasses and crystalline solids provides fresh approaches to problems of long standing in several fields. By introducing fluorescent ions such as UO_2^{++} into different glass bases, the glass technologist has started to interpret their emission spectra and to draw conclusions on the atomic structure and constitution of the glasses (*14*). Such an interpretation is generally based on previous experience with the fluorescence of the same ion present in crystalline material of known symmetry and atomic arrangement. One application is based on the fact that uranium oxide alone is nonfluorescent, but glasses containing traces of uranium can be easily recognized by their strong green fluorescence under ultraviolet light. Uranium, therefore, is used as an indicator to determine the temperature at which glass formation begins.

The most remarkable feature of the activating ability of uranium is that fluorescence will be produced in an otherwise nonfluorescent base when the concentration of the activator is so slight as to escape every formal chemical method of detection; thus, the green to yellow-green fluorescence of the cheap Bohemian glassware of commerce as well as of many silicas has been known indirectly for many years to be due to trace amounts of uranium. It has been only during the last several decades that direct proof has been secured.

In uranium-activated glasses a high melting temperature favors lower valency. Oxidizing or reducing conditions greatly affect the resultant fluorescence, and the presence of water may determine whether a glass or silica containing traces of uranium will fluoresce (*15*); thus, at low temperatures of formation, uranyl compounds can be introduced into glasses, causing fluorescence. But at high formation temperatures, nonfluorescent oxides of uranium will cause fluorescence because of the formation of the U^{6+} ion. The presence of water in a glass containing uranium permits the formation of the hexavalent uranium ion, which results in fluorescence; but a loss of water is coincident with U^{4+} and a lack of fluorescence. Heating such a glass with water and remelting it at low temperatures allows the tetravalent uranium ion to reoxidize and form the hexavalent cation, UO_2^{++}.

Of the many minerals known to fluoresce (*7*), uranium is the activator in the majority of silicas. These silicas include moss agate from Wyoming, hyaline opal from numerous localities, jasper, chalcedony, and various other varieties of hydrated or semihydrated cryptocrystalline silica. The fluorescence characteristic of all these substances is usually yellow to green in ultraviolet light.

FLUOROCHEMICAL ANALYSIS

Aside from the luminescence shown by pure uranyl salts and their solutions, the most sensitive of present-day analytical techniques for uranium rely upon its unusual ability to cause fluorescence in a preponderance of bulk material. While much of our interest in uranium detection and determination lies in mineralogy, the methods of this science can be easily extended to other fields. Uranium is much more toxic than arsenic, and quantities which might escape the usual toxicological approaches would be detected by fluorochemical means with little difficulty.

Representative mineralogical methods, useful in other fields as well, are given in the following sections. Most of these tests are qualitative, but with ingenuity on the part of an investigator, they can be modified for quantitative work.

Mineral Exploration. Ultraviolet light, rendered free of interfering visible wave lengths by means of a suitable filter (*e. g.*, Corning number 9860), may be employed in the field for detecting uranium minerals. When used in conjunction with the more reliable and sensitive bead or solution tests for uranium (described subsequently), rocks containing uranium that would otherwise escape the Geiger-Müller counter may easily be identified.

The primary uraninites—*e. g.*, pitchblende—and the columbium-titanium tantalates are generally nonfluorescent in ultraviolet light. The secondary uranium minerals are frequently brilliantly luminescent. Since the secondary uranium minerals are often associated with the primary ones, their fluorescence may indicate an outcropping of a larger, more valuable body of ore. This is illustrated by zippeite, a secondary mineral found in outcropping pitchblende, the occurrence of the

fluorescent zippeite being due to weathering of the original mineral.

The 1940 investigations of Miexner (*16*) are important in connection with ultraviolet prospecting for uranium minerals. Miexner classified the uranium minerals into (*a*) strongly luminescent, (*b*) weakly luminescent, and (*c*) nonluminescent, according to their response in ultraviolet light. The strongly luminescent uranium minerals include the uranium phosphates, arsenates, sulfates, and others which emit a strong yellow green color. The uranium carbonates fluoresce with more of a green color. The nonluminescent uranium minerals include the silicates and uranium micas whose composition is $M_2(UO_2)_2(XO_4)\cdot nH_2O$, where M may be Cu, Fe, Pb, Bi, Mn, or uranium dioxide; X may be P, As, V, or S; and n may be from 8 to 12.

The nonfluorescent uranium minerals usually have a drab color, often being black or brown. The fluorescent secondary species are usually lighter in color, often a light yellow, and generally have specific gravities approximately half that of the primary ores. Table 2 lists the fluorescent responses of uranium minerals which are usually seen with 2537 A.U. ultraviolet light, such as is generated by the Mineralight.[1]

In prospecting for uranium minerals with the lamp in the absence of reliable tests, it is recommended that known specimens be examined with the lamp before an appraisal of an unknown rock is attempted. Failure to observe fluorescence in uranium minerals in the field may not mean the absence of pitchblende or carnotite, the two most important ores, as indicated previously. Hence, it is strongly advised that chemical tests which are easily employed in the field be relied upon for the final test.

Most uranium ores are attacked by aqua regia or by nitric acid. The few exceptions respond to hydrofluoric acid. In specimens which appear to be uraniferrous—*e. g.*, in view of a high specific gravity and black luster—the fluorescence characteristic may frequently be developed by spotting with acid.

The Zinc Test. The writer (*9, 11, 17*) has developed a simple test for uranium which can be used in conjunction with the ultraviolet lamp. It is essentially a modification of the Buell method (*11*). The procedure is to heat 5 g. of the finely ground mineral sample in 20 ml. of aqua regia for a few minutes, complete solution not being required. This liquid is then diluted with up to 80 ml. of water, depending upon how much of the sample has gone into solution, and several lumps of granular zinc are added. The preparation is then allowed to stand for half an hour, and the zinc lumps removed before they are completely dissolved.

The zinc lumps, while wet, are then gently flamed over a Bunsen burner until a pale yellowish coating begins to form on the surface. At this stage the zinc is allowed to cool and is inspected under the ultraviolet lamp. In the presence of uranium bright yellow to greenish fluorescent spots will be observed over the surface of the metal carrier. If the results are negative, the lump is further heated and, after cooling, reexamined. The uranium spots may exhibit a bluish to greenish afterglow for a few seconds. Care should be taken not to overheat the zinc since it melts rather easily in the flame, although at temperatures of incipient fusion the coating on the zinc will show several color changes if uranium is present. These range from pale yellow through deep yellow, becoming orange, then orange-red, and finally ending in a dark brownish deposit. The variegated colorations correspond to various oxides of uranium which are nonfluorescent. The fluorescent material is of undetermined character, but it appears to be zinc uranyl nitrate or sulfate.

The zinc test is very sensitive, responding to carnotites with less than two per cent uranium oxide present. With the amount of material dissolved from pitchblende by the means mentioned above, it will give quite positive results; however, tests should be conducted with uranium salts and known samples before attempting its use on an unknown. It is convenient to save the lumps of zinc which do show uranium for comparison in subsequent tests. In certain cases the fluorescent specks will appear as bluish hues of yellow or green. These may be taken as positive, but bright blue areas, which are due to reflections on the shiny metal surface, should be disregarded. With a little practice the zinc test will yield reliable results.

The Sill-Peterson Test. Sill and Peterson (*18*), working at the U. S. Bureau of Mines Experiment Station in Salt Lake City, Utah, have developed a simple but reliable fluorescence test for uranium using the Mineralight ultraviolet lamp. They state that the available methods for detecting uranium have lacked one or more of the desired characteristics and that the fluorochemical method is probably more specific and sensitive than the usual qualitative methods for the element. Its speed of application and simplicity make it

TABLE 2

LUMINESCENT URANIUM MINERALS (*16*)

Species	*UV-response*
Strongly Fluorescent	
Autunite	Yellow-green
Beta-uranopilite	Yellow-green
Chalcolite (*cf.* torbernite)	Yellow-green
Johannite (variable)	Yellow-green
Metatorbernite	Yellowish blue
Schroeckingerite (Dakeite)	Green
Torbernite	Yellow-green
Uranocircite	Yellow-green
Uraniferrous hyalite	Yellow-green
Uranophane	Yellow-green
Uranopilite	Yellow-green
Uranospathite	Yellow-green
Uranospinite	Yellow-green
Uranothallite	Green
Medium Strong Fluorescent	
Gummite (variable)	Violet
Beta-uranotil	Yellowish
Schoepite	Yellow-green*
Uranotil	Yellowish
Zippeite	Yellowish

* Indicated by a study now being conducted.

[1] The Mineralight is manufactured in several designs by the Ultra-Violet Products, Inc., 5205 Santa Monica Boulevard, Los Angeles 27, California.

ideal for testing samples prior to quantitative analysis.

The fluorochemical test has been employed over two years by Sill and Peterson on various types of uranium minerals with reliable results. Samples submitted for uranium analysis can be tested at the outset for uranium, and those containing uranium later subjected to the more complicated and accurate quantitative tests. Those not containing the element can be eliminated, thereby effecting a large saving in time and expense. The test has the advantage of using up none of the sample. It is an integral part of the quantitative scheme, so if uranium is found, the analyst can continue with his quantitative determination.

Sill and Peterson took advantage of the observation of De Ment and Dake (*11*) that aqueous solutions of uranium are much more responsive to short wave length ultraviolet light than to the long wave lengths. Their test readily detects as little as 0.3 mg. of uranium at a dilution of one part per million, but if smaller volumes of uranium extract are inspected, the delicacy is greatly increased.

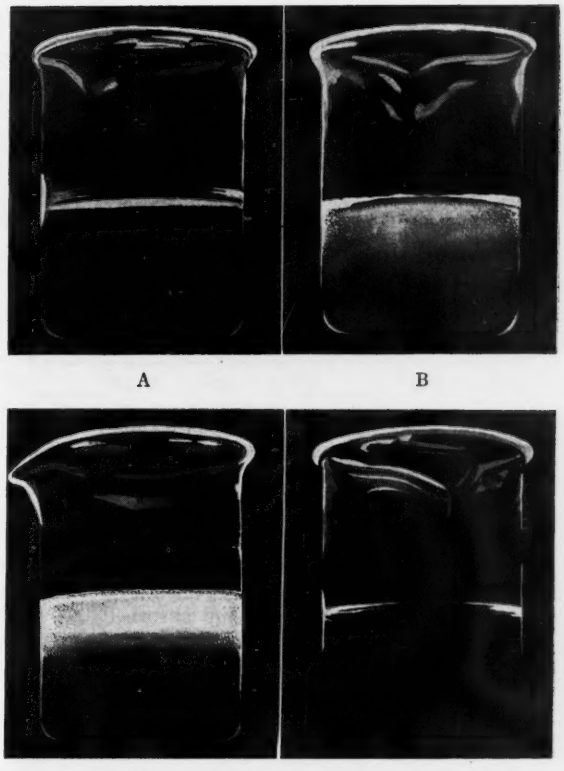
Procedure: Weigh 3 g. of the ore—*e. g.*, low-grade material—into a 400-ml. beaker and dissolve with hydrochloric, nitric, or hydrofluoric acid if necessary. The specimen is dissolved in the same way as in the zinc test described above. To this solution 15 ml. of sulfuric acid are added and the mixture heated until fumes of sulfur trioxide appear. Any dark coloration due to organic material should be removed by the dropwise addition of perchloric acid to the fuming solution. Most of the sulfuric acid is then fumed off by heating, and the liquid is allowed to cool. Dilute with water to 100 ml. and heat until all soluble salts are in solution. Filter, using paper pulp if necessary to give a clear filtrate, and dilute to 150–200 ml.

Ultraviolet Inspection: It is recommended that only the cold-quartz Hg arc (the Mineralight) be employed in inspecting the liquid, since long wave length ultraviolet light does not provide satisfactory results.

The fluorescence observation is conducted in a darkened room, and the eyes of the operator protected with plain, colorless glasses (nonfluorescent) if the inspection is to continue for periods of 15 minutes or more. Pyrex beakers of 400-ml. capacity are chosen for their low fluorescence, and the solutions are placed in these.

The clear solution is placed on a black, nonreflecting background like velvet, and the ultraviolet lamp placed on the open top of the beaker. An inspection cabinet is ideal for such work.

In the presence of uranium the fluorescence will usually be seen as a bright greenish yellow line immediately below the meniscus if the eyes are at the same level as the meniscus and if the solution is viewed at right angles to the incident beam. If the eyes are lower, the entire under-surface of the solution glows greenish yellow. This line, nevertheless narrow, stands out in contrast to the rest of the solution. Such a line is seen when foreign substances are present in the solution, but in solutions that contain no absorbing or quenching materials the fluorescence is distributed more or less throughout the liquid. It may be more greenish than the line described above. With increases in uranium content the volume fluorescence tends to disappear, showing subsequently near the meniscus. This phenomenon not only involves absorption, but also the principle of "concentration quenching" (*cf.* 7).

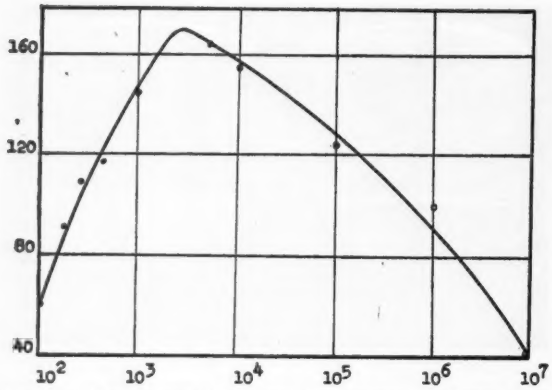


PHOTOGRAPHS TAKEN IN SHORT WAVE LENGTH ULTRAVIOLET LIGHT SHOWING THE FEATURES OF URANIUM FLUORESCENCE

The usual case is shown in *A* comprising a line emission. When the corroborative test is applied, the emission is observed as a volume fluorescence, *B;* but as the uranium content increases, there is a narrowing of the fluorescent area, *C*. Plain water is shown as *D*, the same effect which is obtained in the absence of uranium.

Since certain substances interfere with the uranium fluorescence, the following corroborating test should always be applied to establish definitely the presence or absence of this element: Test the solution as described. If no fluorescence is seen, uranium is not present provided no inhibiting agent is present. Then add about 0.025 *N* uranyl nitrate solution dropwise to the solution under test, stirring after each addition and examining under the lamp. If the fluorescence appears after the addition of a few drops, the conditions for luminescence were favorable, and since no fluorescence was originally observed, it is fairly certain that the original uranium content was not greater than the amount added.

Should the fluorescence fail to appear after several



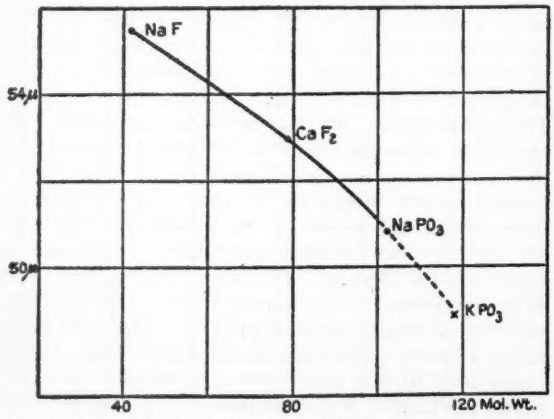
NICHOLS' CURVE FOR MAXIMUM BRILLIANCE, SHOWING THE EFFECT OF URANIUM IN FUSED BEADS OF SODIUM FLUORIDE

The curve is plotted on a log scale, with the abscissae representing mols of solvent per mol of activator (UO_2F_2).

drops of the uranyl nitrate have been added or if it should appear only faintly after the addition of a fairly large amount of uranium solution, it may be assumed either (*a*) that some inhibiting agent is present or (*b*) that the ultraviolet light is being absorbed too completely. The appropriate separations must then be made to eliminate this difficulty before the test can be employed satisfactorily.

On the usual ores such difficulties are rarely encountered, as the method of preparing the sample eliminates most of the interfering substances. Samples containing large amounts of iron may offer some difficulty, especially if large samples are taken to detect small amounts of uranium, owing to a quenching or dimming action. In any event the presence of any interference will be noticed if this test is used, and the analyst can then take the proper steps to eliminate the difficulty.

There are several ions that occasionally inhibit the



NICHOLS' CURVE ILLUSTRATING THE RELATIONSHIP BETWEEN THE WAVE LENGTH OF MAXIMUM BRIGHTNESS AND THE MOLECULAR WEIGHT OF BASES USED IN THE BEAD TEST

The maxima correspond to slightly different colors to the unaided eye, so a sodium fluoride bead will appear lemon-yellow, whereas a borax, calcium fluoride, or sodium phosphate bead will fluoresce green.

fluorescence of uranium solutions, and at certain concentrations may completely destroy it. Likewise highly colored elements, like vanadium derivatives, may obscure the fluorescent line. If continued runs on many samples are to be made, it is advised that reference be given the original report of Sill and Peterson (*18*).

This test has also been used on columbium-tantalum ores, but the sample must be decomposed by pyrosulfate fusion and leaching with dilute sulfuric acid. It has been most helpful in checking separations in the conventional qualitative scheme of analysis. Other applications have been found in studying the amount of uranium occluded by iron hydroxide, and the retention of uranyl ammonium phosphate in the pores of filter paper.

The Fluorescent Bead Test. When small amounts of uranium are fused into an inert base material, they impart a brilliant fluorescence. This fact makes possible one of the most sensitive tests ever devised for an element. The writer has employed the fluorescent bead test in certain of his studies, securing positive results far below the threshold of detection of the usual Geiger-Müller counter.

The fluorescent bead test for uranium dates to 1926 to the observation of Nichols and Slattery (*19*), who noticed that when small amounts of uranium are fused with sodium fluoride and other colorless inorganic compounds, the resulting material exhibits a beautiful lemon-yellow or yellow-green fluorescence under ultraviolet light. They found that the optimum concentration of the activator occurs at a value of one mol of uranium in 2000 mols of sodium fluoride. But the fluorescence can still be seen when one mol of uranium is dissolved in 10 million mols of sodium fluoride.

In the following years the fluoride bead method was developed as a delicate means for both the qualitative and quantitative determination of uranium in a variety of materials. The status of our knowledge has recently been summed by Northup (*20*) in his important contribution to the field.

In his critical study of the bead test for uranium, Northup concluded that the method will detect 0.05 microgram of the element in a single grain of mineral sample. The fluoride bead test is specific except for columbium, which gives a weaker fluorescence of a similar color. To eliminate interference by columbium, Papish and Hoag (*21*) have proposed the use of such bases as potassium fluoride, potassium metaphosphate, and borax. This procedure permits greater specificity, but lowers the limits of detection. Excess cerium and rare earths will also interfere in the sodium fluoride test. These are overcome in minerals containing more than one per cent of uranium by adjusting the ratio of sample to sodium fluoride (*20*). An ether extraction permits the separation of uranium from columbium and rare earths, allowing the detection of 0.0001 per cent of uranium in 0.5 g. of columbite or nonuraniferous cerium minerals.

The actual procedure in the bead test is simple,

consisting of the fusion in a platinum loop of the sodium fluoride or borax with a small amount of the unknown. The bead may be formed in the flame and then dipped in a solution of the unknown, re-fused, re-dipped, re-fused, and so on.

Alkali or alkaline earth element fluorides can all be used in the bead test. A pure, nonfluorescent fluorite proves satisfactory, and borax can be employed. While fine particles of the sample can be fused directly into the bead, the writer recommends the formation of a bead by dipping in a solution of the unknown. After cooling, the bead is examined under long wave length ultraviolet light. Northup (*20*) states that the short waves may excite fluorescence in components other than the U-NaF system, so that the near ultraviolet is best. A preliminary examination of the bead material, without the uranium present, will show whether short waves produce such an effect. An argon bulb or a G. E. H-4 100-watt Hg arc proves satisfactory for exciting the glow. The writer has observed (*9*) that the lemon-yellow fluorescence of the U-NaF bead is produced by all wave lengths of ultraviolet light, and is most intense with high-pressure Hg arcs as well as high-frequency electrical discharges and the radiations from radium.

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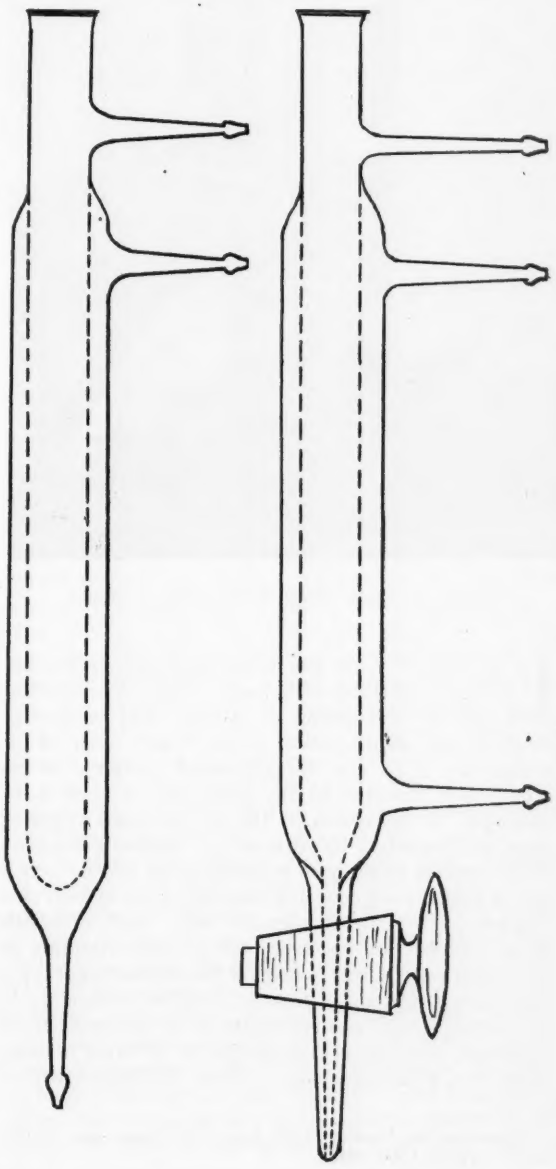
A Condenser-Receiver Unit

S. J. POTEMPA and F. P. CASSARETTO

Loyola University, Chicago, Illinois

A COMBINED condenser, adapter, and receiving flask. Dimensions may be accommodated to macro or semi-micro scale. The side arm of the distilling flask is connected directly. The form with the sealed-in stopcock is especially convenient for fractional distillations.



A Demonstration Mass Spectrometer[1]

W. H. EBERHARDT

California Institute of Technology, Pasadena, California

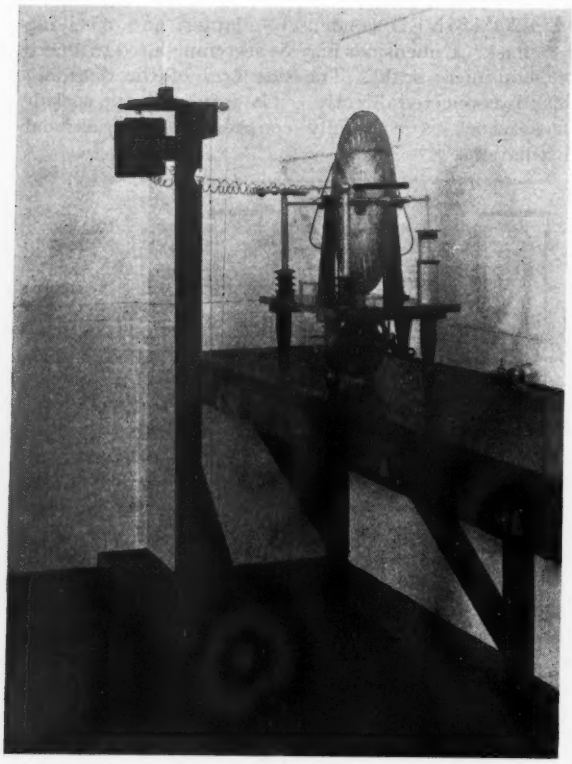


FIGURE 1. PHOTOGRAPH OF MASS SPECTROMETER

IN RECENT years the mass spectrometer has become one of the most important tools in connection with the determination of atomic and molecular weights, and no discussion of this topic, even on an elementary level, may be considered complete unless attention is directed to the principles of mass spectroscopy. A discussion of the conventional types of mass spectrometers based upon the Aston, Dempster, or Bainbridge techniques is complicated by the necessity of introducing concepts relating to the motion of a charged particle in a magnetic field; and, although these concepts are necessary for an understanding of the operation of spectrometers of the conventional type, they do not contribute greatly to an understanding of the value of the mass spectrometer in the problem of analyzing mixtures of components of differing masses. Moreover, a demonstration of these techniques with a model employing macroscopic balls for atoms is essentially impossible because of the very unfavorable ratio of charge to mass which may be obtained with such particles. On the other hand, the velocity selector type of mass spectrometer described by Smythe[2] involves in an understanding of its operation only qualitative ideas of electrostatic attraction and repulsion which are more familiar and intuitively more easily grasped than electromagnetic concepts. In this technique, a beam of ions, which are characterized by various ratios of charge to mass but possess a uniform velocity, is produced by passing a beam of particles with nonuniform velocities through a slit system in a transverse alternating electrostatic field. Only particles with certain velocities determined by the constants of the apparatus and the frequency of the applied field will pass through the slits. The beam leaving the velocity selector may be analyzed by electrostatic or magnetic fields into components of constant ratio of charge to mass, and it is in this analysis that the application of the mass spectrometer to research problems becomes clear. Figure 1.

The technique suggested here is designed to demonstrate with macroscopic particles the analysis of a beam of particles of various masses but uniform velocity into groups of uniform mass. The apparatus is indicated diagrammatically in Figure 2. The particles are dropped starting at rest from the point O and allowed to fall freely under the influence of gravity; thus, although the downward component of the velocity of any particle is not constant along its path, at any point in the path this component of the velocity is independent of the mass of the particle—that is, the velocity of particles in the beam is uniform, but not constant over the path. After falling through the short distance a, the particles pass through an electrostatic field maintained between the plates P and P'. As they enter this field, they fall near the sharp tip of a bullet-shaped piece of metal, B, soldered to one of the deflecting plates, P, and pick up a charge from the corona discharge from this point. Because of this charge, which is of the same sign as that on the plate P, the particles receive a horizontal component of velocity as they pass through the field. After leaving the field, the particles fall freely in a parabolic orbit until they are caught by some collector at the end of their paths. An analysis of the motion of particles in the apparatus is quite straightforward and results in the following expression for the displacement, s, in terms of the dimensions of the apparatus as indicated in the figure, the potential, V, applied to the

[1] Contribution Number 1030 from the Gates and Crellin Laboratories of Chemistry.

[2] SMYTHE, W. R., AND J. MATTAUCH, *Phys. Rev.*, **40**, 429–33 (1932).

plates, and the charge, e, picked up by the balls falling through the corona discharge:

$$s = Ve/dmg\{2a + b - 2\sqrt{a(a+b)} + 2(\sqrt{a+b} - \sqrt{a})(\sqrt{a+b+c} - \sqrt{a+b})\}$$

It will be seen that for a constant applied potential, V, the displacement is proportional to e/m. If the potential remains constant, the charge picked up by the particles from the corona will be constant, providing the particles are of the same size and shape, and the displacement will be inversely proportional to the mass of the particles; hence, a mixture of balls of different masses but the same size and shape may be separated into groups of the same mass by spacing collectors at positions corresponding to various values of the displacement, s, from the position $s = 0$ where the balls will fall if no deflecting potential is applied.

For atoms we have used wooden balls which are approximately spherical, about one-half inch in diameter, and which weigh about one gram. It is desirable to select from a large number of balls those which have nearly the same mass in order to get resolution as sharp as possible. For heavier atoms, holes are drilled through the center of these balls and filled with Wood's metal, the size of the hole determining the final mass of the ball. The deflecting plates are sheet metal about five × six inches in size, with the edges and corners rounded to reduce corona as far as possible. The plates are mounted on a sheet of lucite which serves as an insulating spacer, three and one-half inches wide, and which is fastened by a strut onto a backboard which supports the dropping mechanism and the rest of the apparatus. The "bullet" is a short length of one-quarter-inch brass rod turned to a sharp point on one end and rounded on the other. It will be observed from the diagram that the plates are mounted asymmetrically with respect to the paths of balls falling freely in the absence of a deflecting field. Such an asymmetrical mounting allows a higher field strength to be maintained for a given spacing of the plates and applied potential and is desirable since the balls are deflected only in one direction. Care must be taken in the design of the device to see that adequate spacing of the deflecting plates is allowed so that balls exhibiting the maximum displacement desired will not hit the deflecting plates. The dimensions of the apparatus we have found convenient may be enumerated with reference to Figure 2 as a = one and one-quarter inches, b = six inches, c = four feet, and d = three and one-half inches. The maximum displacement observed is about one foot. None of these dimensions is critical, and it is clear that an apparatus may be designed to fit just about any desired circumstances.

The requirements as to potential are difficult to estimate precisely but are easily filled by a Wimshurst Machine. The potential developed by such a machine is very much more than adequate to operate the spectrometer providing leakage is minimized. Since both deflecting plates are insulated by the lucite separator,

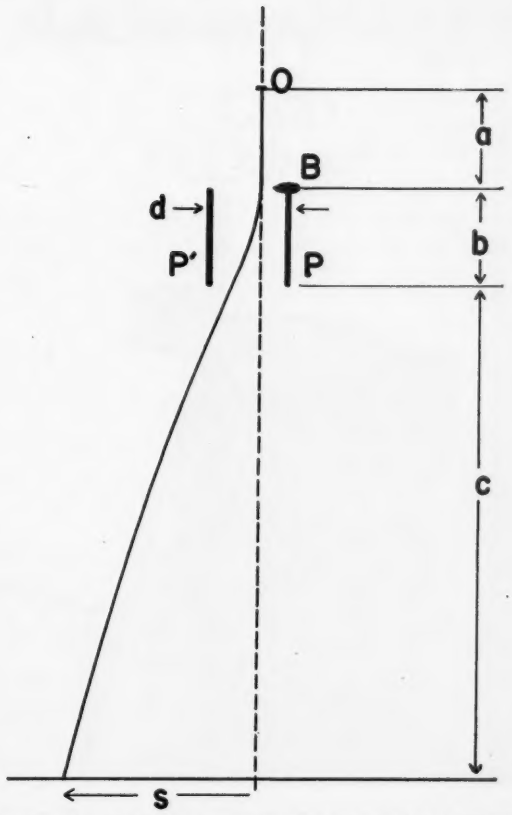


FIGURE 2. SKETCH OF ESSENTIAL DETAILS OF MASS SPECTROMETER SHOWING PATH OF A DEFLECTED BALL. THE SYMBOLS ARE EXPLAINED IN THE TEXT

both from each other and from the ground, and since the charging may be accomplished by allowing the balls to fall through the corona, no difficulty should be experienced from leakage. It will be found that the potential developed by the Wimshurst Machine increases rapidly at first as the rate of revolution of the discs increases, but when the corona discharge commences, the potential increases very much more slowly with increase in the rate of revolution; hence, when the corona appears and is sufficient to charge the balls, it is quite easy to maintain the voltage applied to the system constant by maintaining the rate of revolution of the discs of the generator approximately constant.

The major difficultly in the use of the device consists in dropping the balls individually with no velocity in any direction at the time they are dropped. A simple solution to the problem may be obtained if no attempt is made to make the feeding automatic. A hole large enough to accommodate a ball is drilled in a sheet of wood or lucite about one-quarter inch thick, and the sheet is fastened at the top of the backboard so that the hole corresponds to the path of undeflected particles. A lever is arranged so that the ball is kept from falling when the lever is under the hole, but is allowed to fall when the lever is swung aside. The balls must be

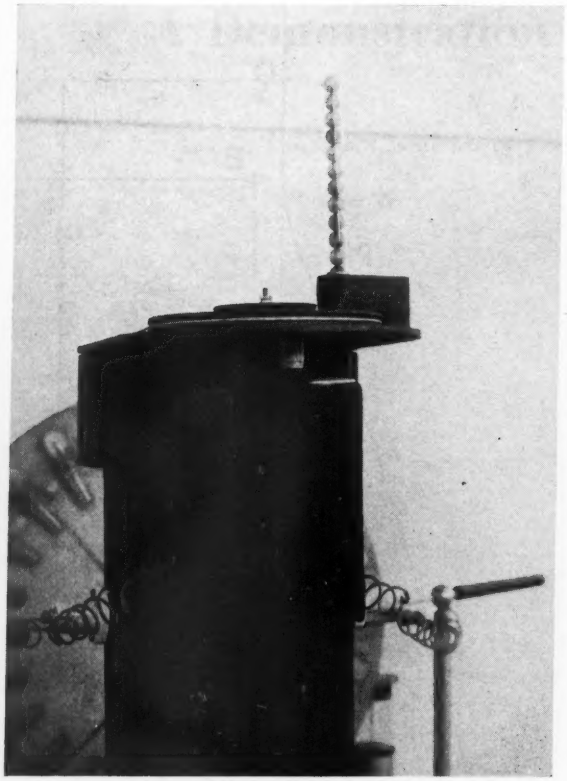


FIGURE 3. DETAIL OF DROPPING MECHANISM AND DEFLECTING PLATES

loaded and released individually and may be conveniently guided to the hole by a stemless funnel placed on top of the plate. Although this system is simple and adequate, it is considered desirable that many balls may be loaded at one time and then automatically dropped individually. See Figure 3.

One device for accomplishing this purpose consists of a rotating disc which picks up a ball at one point of its revolution and drops it at another through a hole appropriately located with respect to the deflection plates. A sheet of wood (the "base sheet") containing this hole is mounted on top of the backboard in a plane parallel to the ground. The disc rotates on this base sheet about a point such that four holes symmetrically drilled in the disc come consecutively over the hole in the base sheet through which the balls drop. A feeding device, consisting of a vertical tube containing the balls one on top of the other, is located over another point of the disc so that the balls are dropped into the holes in the rotating disc as these holes come into position under the tube. The disc is about one-quarter inch thick, so that only one ball at a time may fall into a hole and is so spaced with respect to the base sheet that the ball rolls on the base sheet while it is being carried to the hole through which it is dropped. The disc is driven by a belt-and-pulley arrangement from a motor located on the ground. If this arrangement alone is attempted, it will be found that the balls still have a small component of velocity in the direction tangential to the disc at the time the ball is dropped. This component may be nullified if a short tube, about one inch long, made by winding paper about a cylindrical form, is fixed to project downward from the hole through which the balls drop. If the disc is rotated reasonably slowly so that the balls drop at a rate of about one per second, good results may be obtained with this device.

A collector which will catch the balls at the end of their paths and keep them segregated according to the displacement that they have experienced offers little difficulty. We have used a glass-fronted box equipped with suitable partitions to divide the box into sections about two inches wide. The partitions are sharpened on their top edges to minimize as far as possible scattering of the balls by collisions with these regions. The floor of the box is slanted so that the balls roll toward the glass front to aid in observing the results of an experiment, but it is hinged at the front and provided with a lever so that the direction of slant may be reversed. Under this circumstance the balls roll toward the back of the box and into a channel which empties out of the side of the box so that they may be recovered easily. In order to prevent the balls from bouncing out of the box, the floor of the box is covered with an easily compressed, nonelastic material, such as is used for packing fragile articles; but, to allow the balls to roll easily and freely, this material is covered with a layer of moderately stiff paper.

The author wishes to express his thanks to Professor Linus Pauling and Mr. David Hagelbarger for their interest and valuable suggestions in the design and construction of this demonstration mass spectrometer.

"While the practical aspects of the sciences are not to be despised, their significance lies not so much in the multiplicity of inventions, which make the world so different and life so much safer and easier than it was a century ago, as in the subtle conception which gave birth to these gadgets and which is vastly encouraged by their use—man's confidence in his intellectual supremacy over nature. And what could be more profoundly a matter of the spirit than that?"—L. W. Taylor, in the Scientific Monthly

The Anomalous Behaviour of LIQUID HELIUM II

SIMON A. WEISSMAN
Brooklyn Technical High School
Brooklyn, New York

INTRODUCTION

THE startling results obtained from work done on liquid helium in recent years have caused interest to shift from the study of superconductivity and production of extremely low temperatures by magnetic means (Debye-Giauque effect) to this strange and remarkable liquid. This paper will attempt to describe a few of the unusual properties of liquid helium as exhibited in numerous experiments, and present some theoretical interpretation of the unexpected results.

Kammerlingh-Onnes in 1908 liquefied helium gas using the Linde method. Helium gas, compressed to 100 atmospheres, was cooled to −259°C. by the use of liquid hydrogen. The gas was further cooled by expansion and became liquid. Liquid helium can be cooled further by evaporation. A limit is reached by this method because the vapor pressure diminishes exponentially as the temperature decreases. When the number of molecules which evaporate is so small that the heat of evaporation just balances the inflow of heat, no additional lowering in the temperature can be achieved. By the use of liquid helium, Keesom,[1] working at Leiden and following the procedure described above, succeeded in reaching 0.71°K. At this temperature the vapor pressure is so small that it is impossible to reduce the temperature of the liquid helium any further. Liquid helium requires a pressure of 30 atmospheres to solidify it, which was done for the first time in 1926 by Keesom.[2]

In general, cooling by evaporation of liquids at room temperature is not very efficient since a container for high pressures at room temperatures has a thermal capacity that is always large compared with that of the gas. At low temperatures, however, the situation changes, since according to the gas laws a much larger volume of gas can be compressed into a given container, and the specific heats of all solids drop with temperature, disappearing on approaching absolute zero. We may therefore disregard the thermal capacity of the container, thus obtaining the ideal condition of working with mathematical walls.

The properties of helium have been extensively studied. One unexpected discovery is that there are two kinds of helium. So pronounced is the difference in properties of liquid helium above and below 2.19°K. that the two states have been designated by Keesom as helium I and helium II for the warmer and colder liquids, respectively. Helium I is the liquid as it first forms at a temperature of 4.2°K. The transition point is called the "lambda point" of helium. Although the transition does not seem to be accompanied by latent heat, some authorities[3] have considered it, in some respects, a change of phase. The density, thermal conductivity, compressibility, viscosity, expansion coefficient, dielectric constant, and specific heat of the liquid show abrupt changes in the neighborhood of the lambda point. The reasons for these abrupt changes are not yet fully understood. Among these changes let us consider for the moment that of expansion.

Expansion: The coefficient of expansion of liquid helium shows a discontinuity at the transition or lambda point (2.19°K.). For helium I, under its vapor pressure, it shows the abnormally high value of 0.0222 per degree, and for helium II it is −0.0426 per degree.[4] Therefore the expansion coefficient for liquid helium I is positive and for liquid helium II, *negative* for all temperatures! As a result, an adiabatic expansion will be accompanied by an *increase* in temperature.

Density: For each pressure to which liquid helium may be subjected it has a maximum density at a definite and characteristic temperature. Under a pressure of one atmosphere and at a temperature of 4.2°K., its density is 0.125 g./cm.^{3} or about one-eighth that of water. Under one atmosphere of pressure its maximum density is 0.1473 g./cm.^{3} and is reached at 2.178°K.[5] It has also been shown that helium can be kept in the *solid* state only under a pressure of 30 atmospheres.

Specific Heat: The property of specific heat also shows startling anomalies. According to the measurements made by Keesom and Keesom[6] on the specific heat of helium (under its saturated vapor pressure), there is a variation ranging from the value of *more than 3* at 2.19°K. (the lambda point) to a value of about 1.1 within a temperature interval which is certainly not more than 0.02 degree, very probably much less. This is shown in Figure 1. From measurements of the heat supplied and the temperature increase, they have reached the conclusion that there is no latent heat connected with the lambda transformation. This experiment also indicated a sudden change in the heat conductivity in passing from helium II to helium I.

Compressibility: Thermodynamic theory predicts a relationship between the discontinuity in specific heat, expansion coefficient, and compressibility. It was natural, therefore, to expect a discontinuity in compressibility, too, near the lambda point. The com-

[1] KEESOM, W. H., *Proc. Acad. Sci. Amsterdam, No. 219a*, **35**, 136 (1932).
[2] KEESOM, W. H., *Leiden Comm., No. 184b*, 17 (1926)
[3] MCLENNAN, J. C., *Proc. Roy. Soc. London (A)*, **152**, 1 (1935).
[4] KEESOM, W. H., *Leiden Comm. Suppl., No. 75a*, 20 (1933).
[5] KEESOM, W. H., AND A. P. KEESOM, *Leiden Comm., No. 224d*, 14–20, *No. 224e*, 21–4 (1933), *No 240b*, 1–13 (1936).
[6] KEESOM, W. H., AND A. P. KEESOM, *Physica*, **2**, 557 (1935)

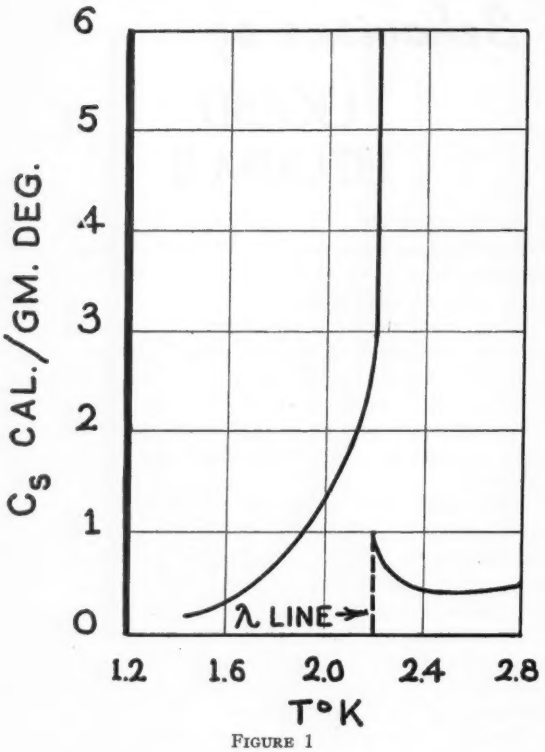


FIGURE 1

pressibility of any liquid can be found from measurements of the velocity of sound in the liquid. The velocity of sound in helium I and II was therefore determined.[7,8] Standing waves were set up between a vibrating quartz crystal and a brass reflecting plate. The reflector was moved and the existence of standing waves was shown by a resonant reaction on the vibrating crystal. Sharp resonance peaks were obtained in both helium I and II, as shown in Figure 2. The velocity at points not too close to the lambda line agrees approximately with values calculated from adiabatic elasticities estimated with the aid of entropy relations.[9,10] Measurements, in which the helium was subjected to a pressure of from one to five atmospheres, show distinct discontinuity at the lambda point.

Thermal Conductivity: Another remarkable property of helium II is its high thermal conductivity. Keesom[11] and his coworkers measured conductivities of 810 cal./-degree cm. sec. This is more that 800 times that of copper at room temperature! Similar results were obtained by Allen[12] and his coworkers. Another anomaly noted was that the conductivity appeared to *increase* ,while the bore of the conduction capillary *decreased.*

Viscosity: The abnormally high thermal conductivity of helium II suggested that the liquid should have an abnormally low viscosity. Now, the viscosity of a liquid may be determined in several ways. A simple method is to allow the liquid to flow through a capillary and then calculate the viscosity from the volume discharged in unit time, the pressure, and dimensions of the apparatus. If helium II is a classical well-behaved fluid, then Poiseuille's formula can be applied. This formula states that the volume discharged in unit time increases with a rise in pressure head and decreases with lowering temperatures.

Data obtained by Allen and Misener[13] on the flow of liquid helium II through long capillaries showed that the viscosity of liquid helium II is about *one-one-thousandth as large as hydrogen gas* which was previously thought to be the fluid of least viscosity! This is of the order of 10^{-9} c.g.s. units. This unusual result will be discussed further under "Transport and Viscosity." Kapitza[14] confirmed the above results using the apparatus in Figure 3. He measured the viscosity by the pressure drop when a liquid flows through a gap between the discs *1* and *2*. The glass tube (*3*) was fixed to the upper disc (*1*). The level of the liquid helium column in the tube (*3*) could be set above or below the level (*5*) of the liquid in the surrounding Dewar flask by means of the thread (*4*). When the separation between the plates (*1* and *2*) was of the order of half a micron (by observation of the optical fringes), the flow of liquid above the lambda point (2.19°K.) could barely be detected over several minutes, while below the lambda point the liquid helium flowed quite easily and the level in the tube (*3*) settled down in a few seconds. Assuming the flow to be laminar, the calculated viscosity is of the order of 10^{-9} c.g.s. units.

Using another standard method for the determination of viscosity, Wilhelm, Misener, and Clark[15] obtained results which are strikingly different. They observed the damping motion of a cylinder executing torsional oscillations about its axis while immersed in the liquid contained in a coaxial cylinder. For helium I at 2.3°K. they observed a viscosity of 2.7×10^{-4} c.g.s. units, while for helium II at 2.2°K., they observed a viscosity of 3.3×10^{-5} c.g.s. units. Obviously the results of this experiment differ from the results of Allen and Misener and also of Kapitza by a factor of 10,000! Since both systems of measurement are equally valid, it becomes imperative to explain the discrepancy in results.

Transport and Viscosity: The following phenomenon observed by Kammerlingh-Onnes[16] in 1922, which in itself is extremely interesting, will help to explain certain discrepancies in the preceding results and of the work which is to follow. He found that the surfaces of

[7] BURTON, E. F., *Nature*, **141**, 970 (1938).
[8] PITT, A., AND W. J. JACKSON, *Can. J. Research*, **12**, 686 (1935).
[9] KEESOM, W. H., AND A. P. KEESOM, *Physica*, **1**, 128 (1933).
[10] KEESOM, W. H., AND A. P. KEESOM, *Leiden Comm. Suppl., No. 76b*, 1–6, *No. 76c*, 1–6 (1938).
[11] KEESOM, W. H., A. P. KEESOM, AND B. F. SARIS, *Physica*, **5**, 281 (1938).
[12] ALLEN, J. F., R. PEIERLS, AND M. Z. UDDIN, *Nature*, **140**, 62 (1937).
[13] ALLEN, J. F., AND A. D. MISENER, *Nature*, **141**, 75 (1938); **142**, 643 (1938).
[14] KAPITZA, P., *Nature*, **141**, 74 (1938).
[15] WILHELM, J. O., A. D. MISENER, AND A. R. CLARK, *Proc. Roy. Soc. London (A)*, **151**, 342 (1935).
[16] DAUNT, J. G., AND K. MENDELSSOHN, *Nature*, **141**, 911 (1938).

two volumes of liquid helium in two concentric vessels adjusted themselves automatically to the same level. Daunt and Mendelssohn, upon further investigation of this phenomenon, found that when an empty beaker was lowered into the liquid, it filled up to the level of the bath although the rim of the beaker was everywhere above the level of the liquid.

When the beaker was partly lifted out of the bath, the level of the liquid in the beaker fell at the same rate as it rose and the level of the bath rose until both had reached the same height. In order to establish whether the transfer took place by distillation through the gas phase or by transfer over the surface, the effect was examined by introducing wicks of twisted copper wire which increased the surface leading from one level to the other. It was found that this increased the rate of transfer to several times the previous rate, but only so long as the wick reached into the liquid at the higher level. When the beaker (without a wick) was lifted completely out of the bath, it was found that the liquid had vanished at the same rate as when it was still partly dipping into it. This was accounted for when it was observed that the liquid collected in drops at the bottom of the beaker and dripped into the bath. The rate of transfer increased rapidly with decreasing temperature. If any of these phenomena occur above the lambda point, the rate is so slow that they could not be observed in this experiment.

These experiments appear to show that the surface of a solid in contact with liquid helium II is covered with a helium film through which the liquid is transferred to the lowest available level. The rate of transfer on glass (it was found to be much higher than on copper) appears to be of the order which one would expect if a monatomic layer were to move with the average kinetic velocity of the molecules. But the fact that the rate of transfer increases rapidly with *falling* temperatures seems to indicate that the phenomenon depends not so much on the molecular velocity as on the viscosity which decreases as the temperature falls. The thickness of the helium film on which the transfer takes place was determined[17] directly by the amount of liquid deposited on a known surface. It was found to be 5×10^{-6} cm. thick.

Having briefly considered the curious phenomenon of creeping films, we are in a better position to understand the discrepancy in the viscosity measurements. It now seems fairly certain that the extremely low viscosity measurements of the order of 10^{-9} c.g.s. units obtained by Allen and Misener were due to the fact that some of the liquid helium was transferred *outside* the capillary by the surface film. An experiment performed by Daunt and Mendelssohn,[18] in which their apparatus was arranged as in the experiment of Allen and Misener, but in which the transport phenomenon was eliminated, disproved the results obtained by Allen and Misener.

[17] DAUNT, J. G., AND K. MENDELSSOHN, *Nature*, **142**, 475 (1938).

[18] DAUNT, J. G., AND K. MENDELSSOHN, *Nature*, **142**, 72 (1938).

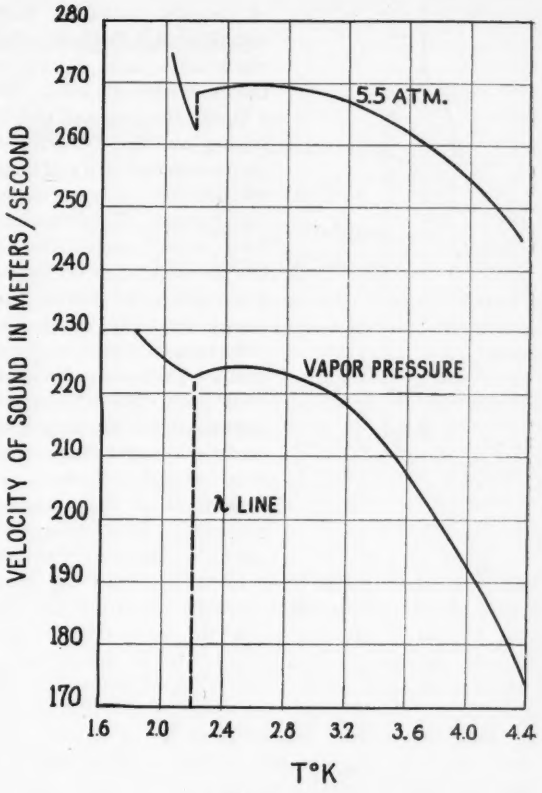


FIGURE 2

According to the results of Daunt and Mendelssohn, the reservoir used by Allen and Misener would have fallen at the rate of 0.02 mm. per second at 2.17°K. due to the transport over the surface of the tube. The actual flow through the capillary tube was therefore negligible.

Suggested Explanations for Some Properties of Helium II: Naturally, the peculiar phenomena and the discrepancies which have been observed brought forth various explanations. Several theories have been put forward to explain the peculiar properties of helium II, and although the weight of evidence in favor of any is not very great, none has been disproved. Recent investigations on the structure of liquids[19] seem to indicate that our concept of random molecular motion needs revision. A solid is pictured as a lattice made up of atoms, held in positions of equilibrium by elastic forces. The relative position of the atoms and the distance between them were determined by X-ray analysis. As the atoms move away from their mean position, they are subjected to restoring forces which cause them to return and continue oscillating about a definite fixed position. The fact that solids diffuse so slowly would indicate that the chance of an atom to leave its fixed position is extremely rare. The theory of the structure

[19] MOTT, N. F., AND R. W. GUERNEY, "Physical Society Reports on Progress in Physics," Cambridge University Press, London, 1939.

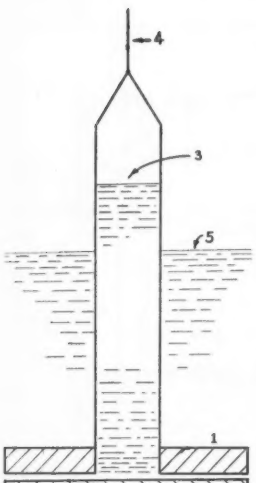


FIGURE 3

of liquids indicates that its molecules behave very much in the same way as do the molecules of a solid. In a liquid, the forces of neighboring molecules confine a given molecule in a cell from which it may only occasionally escape. X-ray studies have shown regularity in the arrangement of liquid molecules. It would appear, therefore, that the difference between a solid and a liquid is not between order and disorder, but in the duration of the imprisonment of the molecule. The only disorder present in helium II is that due to thermal vibrations. We should therefore expect helium II at very low temperatures to have the same degree of order as a crystalline solid in spite of the fact that helium II appears to be the most mobile fluid known. Keesom,[11] attempting to explain the phenomenon of super heat conductivity of liquid helium II, calls attention to the fact that the structure of liquid helium II, which apparently follows from X-ray studies, is a very open one. As a matter of fact, in that structure there are channels which would allow ample passage to the helium atom. Starting from the lambda point and decreasing the temperature, the channels will continually develop, or rather will be regularly less disturbed by moving atoms, and as a consequence heat conductivity increases.

According to the Bohr theory, the energy levels are given by $E = nh\nu$ where n is an integer, h is Planck's constant, and ν the frequency of the radiation. Quite independently, wave mechanics and matrix mechanics both give the same energy levels—namely, $E = (n + {}^1/_2)h\nu$. The only difference lies in the fact that the whole term diagram of quantum mechanics is displaced relative to that of Bohr's theory by half a quantum of energy. This difference, though not exhibited in the spectrum, is very important in problems dealing with the ground state (this is the lowest state where $n = 0$). The ground state therefore possesses a finite energy, $E = h\nu/2$. This is the so-called "zero-point energy." Absolute zero in classical theory is characterized by the fact that the particles are at rest and therefore the mean kinetic energy vanishes. According to wave mechanics, however, the lowest energy is $E = h\nu/2$.

The helium atom contains an even number of elementary particles and would obey the Bose-Einstein statistics. The important aspect of this type of statistics is that the presence of one or more particles in a given energy level increases the probability of another particle occupying the same level. At absolute zero all the particles would concentrate in the lowest energy level. This is known as a Bose-Einstein degenerate gas.[20]

Liquid helium II is pictured as consisting of a great many "condensed" atoms in the ground state—that is, a "super fluid" of no viscosity—and a few atoms in high energy states—in other words, a "gas." Due to the small mass and the weak interatomic forces in helium, the zero-point energy is large, and it is this large energy at the absolute zero which gives liquid and solid helium their large compressibilities and small density. The rapid flow of the helium in the viscosity experiments is then accounted for as due to the transport, with negligible resistance, of the condensed degenerate atoms in the ground state through the other atoms of the liquid. The discontinuity in specific heat can be explained by assuming that only local order of the atoms exists in helium I and large range order exists in helium II.

The density of liquid helium is so small that even on the assumption of a cubic face-centered lattice the distances between molecules are big enough to allow a molecule to move through the system. It is now conceivable that the heat conductivity can be described as a transfer of energy by molecules carrying an energy above the average moving from one wall to another without being able to exchange their momentum or energy with the other intervening molecules.

Heat flow and fluid flow are, however, closely bound together and are further complicated by the transfer of helium II in the form of surface films on every surface immersed in the liquid. This means that although the experiments on the problem are quite simple and classical in type, they are invariably exceedingly difficult of true interpretation.

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[20] BORN, M., "Atomic Physics," G. E. Stechert and Company, New York, 1936.

In order to introduce a new idea into the mind of man, it is generally necessary to eject an old one. To move in new furniture, one has first to move out the old.

All through the history of science we find that new ideas have to force their way into the common mind in disguise, as though they were burglars instead of benefactors of the race.—E. E. Slosson

Percentage Composition AND THE Atomic Theory

R. K. MCALPINE

University of Michigan
Ann Arbor, Michigan

THE relation between percentage composition and the atomic theory as it appears in most of the introductory textbooks in chemistry today seems to be as follows: Given the formula of a compound and the proper atomic weights, it is possible to calculate the percentage composition of the compound; or, given the percentage composition and the atomic weights, it is possible to calculate the simplest formula of the compound. Actually, however, it is possible, by examining the facts of percentage composition of certain series of compounds, to develop a simplified form of an atomic theory, and, by consideration of certain other sets of experimental data, to show why this was modified by steps to its present, modern form.

By chemical analysis, without regard to chemical formulas and atomic weights, it may be shown that ferric oxide, cupric oxide, lead oxide, and hydrogen oxide (water) have the following compositions:

Ferric oxide: 69.94% iron, 30.06% oxygen
Cupric oxide: 79.89% copper, 20.11% oxygen
Lead oxide: 92.83% lead, 7.17% oxygen
Water: 11.19% hydrogen, 88.81% oxygen

From these data it may be calculated that the amount of each positive element that would be found in combination with 100 g. of oxygen is, respectively, as follows: iron, 232.7 g.; copper, 397.3 g.; lead, 1294.8 g.; and hydrogen, 12.60 g. In terms of oxygen = 100, the combining weights of these positive elements would become the numbers just given.

If the chlorides were prepared from the above oxides and their composition accurately determined the following results would be obtained:

Ferric chloride: 34.42% iron, 65.58% chlorine
Cupric chloride: 47.27% copper, 52.73% chlorine
Lead chloride: 74.50% lead, 25.50% chlorine
Hydrogen chloride: 2.764% hydrogen, 97.25% chlorine

When these data are used to calculate the combining weights of iron, copper, lead, and hydrogen on the basis that chlorine = 100, the following values are obtained: iron = 52.49, copper = 89.65, lead = 292.2, and hydrogen = 2.842.

These figures differ obviously from those obtained on the basis that oxygen = 100; however, when the figures in the two series are examined and compared in more detail, it may be observed, first, that the positive elements are placed in the same order in the two lists and, second, that the values in the two series bear a simple relation to each other. This latter fact may be seen if one divides each value in the oxygen series by the corresponding value in the chlorine series.

Iron.....232.7/52.49 = 4.433
Copper.....397.3/89.65 = 4.432
Lead.....1294.8/292.2 = 4.431
Hydrogen.....12.60/2.842 = 4.433

The close similarity in these ratios suggests that if the values in the two series are recalculated in terms of one of the positive elements, essentially identical figures would be obtained. Since hydrogen has the lowest value in the two series it may be set up as the standard and assigned an arbitrary value of 1.000. On this basis the following numbers are obtained:

	Oxygen series	*Chlorine series*	*Average*
Hydrogen	1.000	1.000	1.000
Oxygen	7.937	...	(7.937)
Chlorine	...	35.24	(35.24)
Iron	18.47	18.49	18.48
Copper	31.53	31.59	31.56
Lead	102.75	102.96	102.85

It is now evident that in the formation of both oxides and chlorides, the positive elements under consideration combine with the oxygen and chlorine in characteristic unit bundles of mass, and, so far as these data go, the relative weights of these unit masses may be represented by the figures in the last column of the table.

These facts present the fundamental basis for the atomic theory. This theory offers a mechanism of chemical reaction that is consistent with the facts given, suggesting that each element is composed of unit bundles of material called atoms, that the atoms of a given element all have the same mass, that the relative masses of atoms of different elements are as shown in the table, and that chemical reaction consists in the union or separation of atoms. It should be noted that the law of definite proportions, which deals with the constancy of composition of individual compounds, does not of itself lead to an atomic theory. It is only when the composition of analogous series of compounds is studied that the idea of unit bundles of weight, or atoms, suggests itself. If there were no simple relation between combining weights in terms of oxygen and combining weights in terms of chlorine, there would be no chemical atomic theory.

On the basis of the combining weights thus derived, and by assuming that the symbol of each element represents its combining weight, it is a simple matter to derive formulas for the different compounds from their percentage compositions. Thus, if the percentage composition of ferric oxide is 69.94% Fe and 30.06% O, and the symbols Fe and O stand for 18.48 and 7.937, respectively, the composition of ferric oxide by symbol weights is obtained as follows:

symbol wts. Fe: symbol wts. O = 69.94/18.48: 30.06/7.937

When the indicated divisions are carried out, they give

the numbers 3.78 and 3.79. These are so nearly identical that it requires no stretch of the imagination to say that the ratio is 1:1. On that basis the formula for ferric oxide is FeO, a formula which, with the weights for which the symbols stand, represents the composition of the compound with the same accuracy as does the modern formula with modern atomic weights. Corresponding calculations for the other formulas give the following: cupric oxide, CuO; lead oxide, PbO; water, HO; ferric chloride, FeCl; cupric chloride, CuCl; lead chloride, PbCl; and hydrogen chloride, HCl.

A number of these formulas are different from those to which we are accustomed today, and thus it becomes evident that there are other experimental facts to be considered. Even in the matter of percentage composition of oxides of the positive elements under examination, there is another chapter to be written. These positive elements form another series of oxides of different percentage composition.

Ferrous oxide: 77.73% Fe, 22.27% O
Cuprous oxide: 88.82% Cu, 11.18% O
Lead peroxide: 86.62% Pb, 13.38% O
Hydrogen peroxide: 5.927% H, 94.07% O

If symbol weights are calculated from these new data on the basis H = 1 and O = 7.937 (except for hydrogen peroxide), the following numbers are obtained: H = 1, O = 15.87 in hydrogen peroxide, Fe = 27.70, Cu = 63.13, and Pb = 51.38. On comparing these with the previous series of values it is found that fairly simple relations can be set up between the two sets of figures.

Oxygen.....15.87/ 7.937 = 1.999 = approximately 2
Iron.....27.70/ 18.48 = 1.498 = approximately 1.5 (or $^3/_2$)
Copper.....63.13/ 31.56 = 2.0003 = approximately 2
Lead.....51.38/102.85 = 0.4994 = approximately 0.5

From these facts it is a simple matter to set up new values for the symbol weights such that the composition of the compounds in both series may be properly represented by simple formulas. In each case the greatest common divisor of the two numbers will be taken as the symbol weight of each element. With copper, lead, and oxygen this merely involves using the smaller of the two numbers, but with iron the symbol weight now becomes half the smaller value or one-third the larger. The new symbol weights thus become: H = 1, O = 7.937, Cl = 35.24, Fe = 9.24, Cu = 31.56, Pb = 51.38. With these numbers and the percentage composition of the several compounds, the simplest formulas now become:

Ferric oxide	Fe_2O	Ferrous oxide	Fe_3O
Cupric oxide	CuO	Cuprous oxide	Cu_2O
Lead oxide	Pb_2O	Lead peroxide	PbO
Water	HO	Hydrogen peroxide	HO_2
Ferric chloride	Fe_2Cl	Ferrous chloride	Fe_3Cl
Lead chloride	Pb_2Cl	Hydrogen chloride	HCl

It is through the consideration of such formulas, in which one symbol weight of one element shows varying combining capacity for symbol weights of other elements, that the question of valence is first raised. If valence is defined as the combining capacity of one symbol weight of one element for symbol weights of other elements, then an examination of the formulas just listed leads to the following simplest system of valences for the individual elements: H = 1 or 2; O = 1, 2, or 3; Cl = 1, 2, or 3; Fe = 1; Cu = 1; Pb = 1.

Again we are faced with both formulas and valences that are at variance with what is being taught today. Evidently there are still other facts to consider. It is true that the above system of valences is the simplest one that will account for the given facts, but it is also true that it is not the only system that might be used. Consider the case of the two chlorides of iron, for example. These two compounds show marked differences in physical properties and in chemical behavior. Since the formulas suggest that the valence of chlorine is different in the two cases, it is only natural to refer the different properties to the two kinds of chlorine present; but when these properties are examined in detail, it appears that the chlorine is the same in the two compounds and the iron is different. For example, when the two are dissolved in water, one gives a yellow color, the other is colorless; but on treatment with silver nitrate, which precipitates the chlorine, both give the same white precipitate of silver chloride, which, on being filtered out, leaves the colors as before. Or, on treatment of the two solutions with sodium hydroxide, which precipitates the iron, one gives a reddish brown precipitate, the other a white (to gray or black), and both filtrates are colorless. These examples may be multiplied many-fold, but they all point to the same fact—namely, that the differences are in the two forms of iron present rather than in the chlorine.

This raises the question of whether the symbol weights, valences, and formulas can be manipulated in such a way as to set up a system that will correspond more obviously with the chemical facts. The formulas Fe_2Cl and Fe_3Cl are the simplest formulas based on percentage composition and the symbol weights Fe = 9.24, Cl = 35.24. If one wishes to assume that the true symbol weight of iron is some multiple of 9.24, while chlorine remains at 35.24, the following series of formulas can be obtained:

Symbol weight	*Ferric chloride*	*Ferrous chloride*
9.24 × 2	FeCl	Fe_3Cl_2
9.24 × 3	Fe_2Cl_3	FeCl
9.24 × 4	$FeCl_2$	Fe_3Cl_4
9.24 × 5	Fe_2Cl_5	Fe_3Cl_5
9.24 × 6	$FeCl_3$	$FeCl_2$

A consideration of the simplest assumptions of corresponding valences of Fe and of Cl in these two series of formulas will show that it is not until the last two are reached that there is a complete shift from constant valence of iron with variable valence of chlorine to variable valence of iron with constant valence of chlorine. These last formulas, therefore, are the simplest ones that are consistent with the chemical properties as well as percentage composition.

Similar considerations in the case of the chlorides of copper will change the simplest formulas for cupric chloride and cuprous chloride to $CuCl_2$ and CuCl, respectively. When the oxides are studied in the same way, it is found that here, also, the formulas must be shifted to show constant valence of oxygen and varying valence of the positive metal; however, when these new formulas for the oxides are examined, they still look strange, for ferrous oxide is FeO_2, ferric oxide is FeO_3, water is HO, and hydrogen peroxide is HO_2. In other words, the data thus far considered have not suggested that the valence of either chlorine or oxygen should be other than unity, and so far there is no reason for thinking of them as different from each other.

The additional experimental facts that are more easily organized by shifting the valence of oxygen to two are (*a*) a comparison of gram-symbol volumes of hydrogen, chlorine, and oxygen at standard conditions, and (*b*) the ratio by volume with which hydrogen reacts with chlorine as compared with oxygen.

The gas densities of hydrogen, chlorine, and oxygen (grams per liter) are 0.08988, 3.2140, and 1.4290, respectively. When the volume relations are studied in the gaseous reactions, it is found that one volume of hydrogen reacts with one volume of chlorine, but that two volumes of hydrogen react with one volume of oxygen. These last relations are sufficiently simple so that they lead to the idea of unit bundles of volume for gases just as the study of percentage composition leads to the idea of unit bundles of weight. It would be a natural next step to examine the volume relations between gram-symbol weights of the three gases. Using the symbol weights H = 1, Cl = 35.24, and O = 7.937, and dividing each by the density of the corresponding gas at standard conditions, the number of liters of gas per gram-symbol weight may be obtained.

Hydrogen	1.000/0.08988	= 11.126 liters
Chlorine	35.24 /3.2140	= 10.96 liters
Oxygen	7.937/1.4290	= 5.554 liters

It requires very little imaginative effort to see that the gram-symbol volumes for hydrogen and chlorine are nearly identical while that for oxygen is essentially half that of the others. The question then arises, is it possible to manipulate the symbol weight of oxygen (and its corresponding valence) in such a way as to avoid the necessity of considering oxygen as exceptional, both in the volume occupied by gram-symbol weight and in the volumetric ratio with which it combines with hydrogen? Since the symbol weight 7.937 was arrived at merely as the simplest value consistent with the given facts, it is entirely permissible to say that the symbol weight should really be twice that value (with corresponding valence of two for oxygen) if, with additional facts to consider, this offers a simpler method of dealing with all the facts. Thus, if the symbol weight were changed to 15.87, the volume of one gram-symbol weight would become 11.108 liters, which is practically the same as that for hydrogen and chlorine. Doubling the symbol weight would require that the valence also be doubled so that the formulas should represent properly the compositions by weight. On this basis the valence of oxygen in the oxides becomes twice that of chlorine in the corresponding chlorides. This gives the formulas ferrous oxide = FeO, ferric oxide = Fe_2O_3, water = H_2O, hydrogen peroxide = H_2O_2. At the same time, the fact that one volume of oxygen combines with two volumes of hydrogen while one volume of chlorine combines with only one volume of hydrogen is given a simple explanation by saying that the valence of oxygen in water is two while that of chlorine in hydrogen chloride is only one.

One might easily continue the development along these lines, through the adoption of the oxygen standard for atomic weights for reason of the greater accuracy of the experimental ratios, and finally arrive at the modern notions of isotopes, atomic numbers, atomic structure, and varying kinds of valence. For the present, however, it is sufficient to note that there is an enormous amount of confirmatory evidence for the symbol weights and the chemical formulas whose derivations have been worked out along the lines here indicated. Thus, it was possible to organize the elements into the periodic chart by tabulating their physical and chemical properties and studying the variations in these in relation to the symbol weights of the elements. Similarly, electrochemical equivalents, vapor density methods of determining molecular weights, freezing and boiling point studies of solutions, the phenomena relating to ionization, etc., etc., have all been fitted into a consistent scheme developed around the formulas now in use.

Through the whole story there is a certain pattern of things repeated over and over. Certain experimental facts are available, and a simple theory is developed that affords an effective correlation of these facts. Then additional facts become available which may require some modification of the original theory. In the new theory that is developed, the attempt is made to keep it in the simplest form that will effectively account for the known facts. Again new facts are discovered and the theories correspond ngly modified. It will be noted that the old facts must be retained as well as the new ones, but that the unessential parts of the theories may be modified or wholly discarded. And to the extent to which chemistry is a growing science in which new facts are to be discovered, it seems perfectly certain that progress will continue to be made along these same lines. With new instruments and new methods of attack new facts will be discovered, and new theories will then be developed to correlate more effectively these new facts with the old.

Between June 1 and September 1 mail sent to the editorial offices of the Journal should be addressed: JOURNAL OF CHEMICAL EDUCATION, Woods Hole, Massachusetts.

BUST OF BERTHOLLET AT THE TOWN HALL OF ARCUEIL

Claude Louis Berthollet

(1748–1822)

PIERRE LEMAY
Fontenay sous Bois (Seine), France

RALPH E. OESPER
University of Cincinnati, Cincinnati, Ohio

(*Continued from page 165*)

AT THE close of his first Italian campaign Bonaparte forced the subjugated princes to make enormous contributions of choice items from their museums and libraries. The Directory sent a committee, including Monge and Berthollet, to select the paintings, manuscripts, scientific equipment, etc. Berthollet, who, of course, spoke Italian fluently, was appointed head of this group. His report to the *Institut* on the restoration of several Raphaels ("The Transfiguration," "The Virgin of Foligno," etc.) revealed the extent of his competence even in fine arts. The two scientists became well acquainted with Bonaparte who took them almost everywhere with him so that he could hold scientific discussions with them. After the Treaty of Campo Fornio (October 17, 1797) the general engaged Berthollet to give him private instruction in chemistry.

When Bonaparte made up his mind to head an expedition into Egypt, he also decided to take with him a large number of eminent scientists,

> expecting, no doubt, an *éclat* from such a halo of surrounding science as might favor the development of his schemes of future greatness.... His illustrious pupil imparted to our philosopher his intended expedition to Egypt, of which no whisper was to be spread abroad till the blow was ready to fall; and he begged of him not merely to accompany the army himself, but to choose such men of talent and experience as he conceived fitted to find there an employment worthy of the country they visited and of that which sent them forth. To invite men to a hazardous expedition, the nature and destination of which he was not permitted to disclose, was rather a delicate task, yet Berthollet undertook it. He could simply inform them that he would accompany them; yet such was the universal esteem in which he was held, that all the men of science agreed at once, without hesitation, to embark on an unknown expedition whose dangers he was to share with them. Had it not been for the link that Berthollet supplied between the commander-in-chief and the men of science, it would have been impossible to have united, as was done on this occasion, the advancement of knowledge with the progress of French arms.[20]

Berthollet and Monge sailed with Bonaparte on the "Orient" in May, 1798. They went with him to Alexandria, Cairo, into the Syrian desert, and even to St. Jean d'Acre, where the British stopped the French advance. They slept in his tent. Their intimacy with the general was so noticeable that some of the soldiers disliked them because they believed that the scientists had persuaded Bonaparte to undertake this expedition into an inhospitable foreign country, which much of the army had come to detest.

In August, 1799, the political situation at home made Bonaparte decide to return to France, and he invited Berthollet and Monge to go with him. The day of their departure, while waiting to be told when to go abroad, the three were together in Cairo in the gardens of the palace of Esbekich. The general was disappointed by the partial defeat of his expedition, disturbed over what he would find in France, perhaps regretful of the direction in which he had turned his genius. Here, according to Geoffrey Saint-Hilaire, the following dialogue took place:

> "The army as a profession was not to my liking. I only took it up out of a sense of duty. When I was young, I dreamed of becoming an inventor, a Newton!"
>
> "What do you mean, General? Don't you know that Lagrange has said that no one can achieve the glory of Newton? There was only one world to discover..."
>
> "What are you saying? What about the world of minutiae? Who has ever thought of that world? From the time I was 15, I believed in it. I worried myself about it then, and the memory lives in me as a fixed idea that I can never forget.... I am sure

[20] THOMSON, T., *op. cit.*, vol. 2, p. 147. See also P. LEMAY, "*Berthollet en Egypte*," *Le Courrier Médical*, August, 1933, p. 407.

that our friend 'Berthollet the thinker' (he sometimes called him that familiarly), in his knowledge of the play of affinities, is surely not of the same opinion. I ask you, Monge, who has paid any attention to the character of the mutual action, at short range, of the minute atoms of which we involuntarily are to some degree the observers? You, Monge, or your Newton, would you have discovered it?

"Just think: would it not be more splendid, greater, but above all more profitable to humanity, than a philosophical speculation? Newton was satisfied with having solved the problem of motion in general by his discovery of the planetary system: that is magnificent for you clever mathematicians.

"But if I could have taught men the mechanisms of the motion which is communicated to each other by the smallest bodies and which is determined by the interference of those same bodies, I would have solved the problem of universal life; and that done, and I believe it is possible, I should have surpassed Newton by all the distance which separates matter and intelligence. Consequently, there is no truth in your saying of Lagrange, since the world of minutiae remains to be investigated. There is that world, the most important of all, which I had flattered myself that I had discovered; the thought of it fills me with regret and my soul with pain."

Bonaparte's interest in chemistry persisted and, when possible, he resumed the lessons. He came to have absolute confidence in Berthollet's judgment and acquired the habit of attributing many chemical discoveries to him, which annoyed Berthollet greatly. When controversial matters concerning science came to him for decision, or if he received unsatisfactory replies, he frequently said, "Well, I will ask Berthollet."

This esteem and confidence were engendered by an appreciation of Berthollet's intellectual stature and zeal for science. Joined to this was his simplicity of manner. He never lacked courage and refused to compromise with the truth, even when his personal safety was endangered. At the request of the Duke of Orleans, who wished to gain inside information, Berthollet allowed his name to be placed on the roll of the Harmony Lodge. This organization had been founded by the famous imposter Mesmer as part of his campaign to spread the doctrine of animal magnetism.[21] Berthollet, however, resigned from this organization on May 2, 1784, after publicly declaring:

I have attended more than half of the course of lectures delivered by M. Mesmer during April, 1784. I have been admitted to the treatment rooms and crisis chambers, where I made some observations and experiments. I declare that I have not been able to detect any trace of the existence of the agent which M. Mesmer calls "animal magnetism." I have come to a conclusion concerning the doctrine which was expounded to us during the lectures and which is contradicted by truths well established both in daily life and animal behavior. I have witnessed nothing in the convulsions, spasms, and crises, which are claimed to be produced by the magnetic processes (if these untoward events really occur), which cannot be entirely attributed to the imagination, to the mechanical effect of rubbing very sensitive parts, or to the operation of the familiar law that an animal tends to imitate and to place itself, even involuntarily, in the same position in which it sees another animal, a law which convulsive maladies so frequently follow. I declare that I regard this doctrine of animal magnetism and the practice that is based on it as completely chimerical, and from now on, I grant everyone permission to make use of my declaration in any way he may wish.

This forthright statement naturally displeased the fanatical followers of Mesmer, and some of them actually attacked him bodily. Berthollet was exceedingly well built, but despite his strength, it would have gone ill with him if the Marquis de Chastellux had not interfered.[22]

His intrepidity in opposing Robespierre has already been related. In Egypt he showed similar courage and stood up against Bonaparte. The latter often was brutally frank and insulting when things did not go as well or as quickly as he wished. "Bonaparte, you are wrong, and you are being rude." He willingly shared hardships with the soldiers. Out in the desert he gave up his carriage to some wounded men and walked almost 60 miles in the blazing heat. He bravely defended the books and instruments of the expedition for three days when the Egyptians revolted in protest against a new burdensome tax. When the Mamelukes fired on the boat carrying him down the Nile, he calmly filled his pockets with stones "so in case I am killed my body will sink and not be desecrated by these barbarians."

The *Institut d'Egypte*, constituted on the same general plan as the *Institut de France*, was founded by a decree of Bonaparte on the third day of Fructidor, Year 6. The first meeting was held three days later (August 24, 1798) at Cairo in the palace of Hassan Kachef. Its objectives were chiefly utilitarian, and from the start Bonaparte selected most of the subjects to be studied. Each of the topics was assigned to a specially chosen committee which reported back to the *Institut*.[23]

Berthollet was, of course, a leading figure in this organization and was its second president, succeeding Monge. Meetings were held at stated intervals, and papers were read by the various members on the climate, the inhabitants, and especially on the natural and artificial products of Egypt. Berthollet, among other topics, reported on: fuels for bread ovens, substitutes for hops in the manufacture of beer, clarification and freshening of water taken from the Nile, and Egyptian raw materials for gunpowder. Four papers by Berthollet, including one on natural soda, can be found in the "Memoirs of the Institute of Egypt."[24]

In July, 1799, he read to the *Institut* extracts from the manuscript of a book that eventually made notable chemical history. He presented the "*Recherches sur*

[21] F. A. Mesmer (1733–1815), an Austrian physician, came to Paris in 1778. He taught that a subtile celestial fluid could be applied in medicine. He soon built up a following of fantatics, including even the king's brother. The government offered him 20,000 livres for his secret. A committee from the *Académie des Sciences* declared him a charlatan, and explained the cures as self-delusions. His followers thought he was being persecuted and raised 340,000 livres in response to his promise to reveal his secret. When the game was played out, he went to England. His name is preserved in the term "mesmerism," and he must be credited with recognizing the value of psychotherapy.

[22] According to some, this attack occurred during a banquet held by the Mesmerists, while other more plausible accounts state that it was made while Berthollet was peacefully strolling in the garden of the *Palais Royal*.

[23] Because of the murderous attacks by the Arabs, it was unwise to venture out of Cairo without a sizable armed escort. Consequently most of the scientists stayed within the city and devoted themselves to matters connected with the *Institut*.

[24] "*Mémoires sur l'Egypte*," 4 vols., Paris, **1800**. Abstracts of the Proceedings are given in *Ann. Chim.*, **29**, 193 (1799); **33**, 80 (1800).

les Lois de l'Affinité Chimique" before the *Institut de France* when he arrived in Paris, and it was published in 1801.[25] This book was expanded into two volumes that were issued as the now celebrated "*Essai de Statique Chimique*" in 1803.[26]

Crude sodium carbonate had been taken from the Egyptian lakes since earliest times. This trona, or natron ($Na_2CO_3 \cdot NaHCO_3 \cdot 3H_2O$), was used for various chemical purposes and in embalming. There is little doubt that Berthollet's investigation of this product was the origin of his studies that culminated in two discoveries, one practical, the other theoretical. He showed that this salt had been and was still being formed by a double decomposition reaction. According to his theory, the active materials were the saturated brine and the limestone bed of the lake. This reaction between sodium chloride and calcium carbonate had been proposed as early as 1737 by Duhamel as a possible method of preparing sodium carbonate. In 1782 Guyton de Morveau and Carny tried to apply on a commercial scale an analogous reaction, proposed by Scheele in 1775. In this a moistened mixture of salt and lime was exposed to the air; after some time an efflorescence containing sodium carbonate appeared on the surface. The results were not favorable. The $NaCl$-$CaCO_3$ reaction has never been a feasible industrial method, but Berthollet hoped that his studies would pave the way to success because "by this decomposition we will secure the soda required for our glass factories, soap works, and washing compounds."

The ideas of Berthollet, which originated in these studies, were to have considerable significance along another line because they were to prove that the affinity of materials is not simply elective, as Bergman believed, but depend on the conditions of the experiment, and particularly on the respective masses involved. Unfortunately, the statement of his ideas in his books was far from clear. J. B. Dumas (1800–84), the leading French chemist of his time, wrote:

> This book is written in a rather obscure manner. The ideas are excellent and clear, but their exposition is confused and troubled; sometimes it is difficult to grasp them. Quite a few of the passages can be understood only by consulting the writings of his students. What I am saying to you about the "*Statique Chimique*" is not meant to detract from the glory of its author, nor to diminish the lustre that his genius has shed. I can speak freely to you about the form of this work because basically no one admires it more than I do. It occupied my attention almost constantly for three or four years; from the ages of 17 to 21 I read, reread, and meditated on it. Often I blamed myself for not being able to understand it, but I see now that the author was as much at fault as I was. I read it, pen in hand, making extracts, reflecting, commenting. I must confess that this labor, these efforts, have been most useful to me. It was with Berthollet that I trained myself to the study of chemistry. If today I have the privilege of raising my voice in this hall and if you willingly lend me your ears, I can truthfully declare, that to some extent, I owe this to the study I made of Berthollet's "*Statique*."[27]

Berthollet's ideas were about as follows. If two materials, such as potassium sulfate and nitric acid, are brought together by means of a solvent, such as water, the constituents distribute themselves so that the mixture contains some potassium sulfate and nitrate and some free sulfuric and nitric acid. Two salts, such as calcium chloride and potassium sulfate, likewise undergo double decomposition; however, one product will be formed almost exclusively if the exchange of the elements or radicals of the two materials can produce a new compound more volatile or less soluble than the reactants—in other words, if this compound can be removed by volatilization or precipitation; however, if no material is removed, the respective quantities of the various possible compounds depend only on the affinities and on the relative quantities of the original materials. The idea of the mass or quantity of the interactant was thus introduced. If two materials MX and NY interact, the distribution of M and N between X and Y will always be governed both by the direct action of their reciprocal affinities and by their masses. Consequently, if the affinity is slight and the mass considerable, the result may be the same as when the affinity is considerable and the mass small. For instance, in the reaction

$$m\mathrm{MX} + n\mathrm{NY} = (m - x)\mathrm{MX} + (n - x)\mathrm{NY} + x\mathrm{MY} + x\mathrm{NX}$$

if the mass m is increased, the mutual decomposition proceeds to a greater extent, and x, as well as the ratio $x/(n-x)$ increases. Accordingly, if m becomes infinitely large, the fraction x/n tends to become unity. Under such conditions the decomposition is complete, no matter how feeble the affinities of MY and NX.

About 1850 H. Rose studied the hydrolysis of metal sulfides and confirmed Berthollet's views on the significance of mass. Calcium sulfide reacts readily with water, despite the fact that the products, H_2S and $Ca(OH)_2$, have much affinity for each other. Furthermore, the reaction is favored by increasing the quantity of water. Rose also showed that prolonged action of sufficient quantities of carbon dioxide and water will accomplish the decomposition of refractory rocks that resist even strong acids applied in the ordinary fashion.

Another important consequence of Berthollet's ideas is the existence of a limit of double decomposition, *i. e.*, the establishment of an equilibrium. The work of J. H. Gladstone (1855) and Malaguti developed this concept, which was further confirmed by the studies (1863–65) of M. Berthelot and Pean de St. Gilles on the

[25] This volume of 105 pages is now quite rare. A large part of the text was included in the extensive abstract by BOUILLON LAGRANGE, *Ann. chim.*, **36**, 302 (1801); **37**, 151, 221 (1801); **38**, 3, 113 (1801). A translation entitled "Researches into the Laws of Chemical Affinity," by M. Farrell, was published at Baltimore in **1809**.

[26] "Essay on Chemical Statics," translated by B. LAMBERT, London, **1804**. In **1806** Berthollet published a supplement, "*Nouvelles Recherches sur les Lois d'Affinité.*"

[27] DUMAS, J. B., "*Leçons sur la Philosophie Chimique, Professées au Collège de France,*" *Recuilles par* M. BINAU, Paris, **1837**, p. 379. E. G. FISCHER, who issued a German translation of the "*Recherches*" at Berlin in **1802**, said in his preface: "I request those who wish to appraise my labors correctly and justly, first to consult the text of the profound Berthollet in the original. Its study has not been found easy even in France. I freely admit that I was not sure that I had grasped the meaning of many passages until I had worked through the entire book more than once."

formation of esters. In 1867 the Norwegians, C. Guldberg and P. Waage, published their classic paper on the influence of mass on an equilibrium in a homogeneous system and reduced the idea to an algebraic formula. Subsequently, Willard Gibbs, J. H. van't Hoff, and finally Henry Le Chatelier definitely established the law of mobile equilibrium and developed the present-day familiarity with the effects of disturbing influences on systems in equilibrium. In principle all reactions must be regarded as reversible, and hence the importance of the seed planted by Berthollet can hardly be overestimated.

It should be noted that Lavoisier seems to have had at least a faint notion of the concept of equilibrium. In his discussion (1782) on the affinities of oxygen, and again in his "Essay on phlogiston," he hints at the idea.

> An erroneous notion of affinities will be obtained by believing that a substance will always take from another the whole of a principle for which it has more affinity.... It is necessary, therefore, to consider oxygen in those types of decompositions as being subject to unequal forces. On one hand it is attracted by the metal which tends to be converted into a calx, otherwise known as an oxide; on the other hand it is held by the sulfur, and it distributes itself between the two until there is equilibrium; thus, when the table of affinities states that silver, mercury, or copper takes oxygen from sulfur, it does not express the exact truth. It should say that when these metals are exposed to both oxygen and sulfur, the oxygen divides itself between the sulfur and these metals in a certain proportion which leads to an oxide and sulfurous acid.

Berthollet's confusion of homogeneous mixtures (solutions) with compounds led him into a capital error. He stated that substances are capable of uniting in all possible proportions, that the composition of the products is influenced by the relative quantity of the reactants, and that there is no such thing as a definite compound unless it has been produced by some accidental circumstance such as insolubility, volatility, etc. This opinion was at once challenged by the French chemist, J. L. Proust (1755–1826), then Professor of Chemistry at the University of Madrid. He proved eventually that Berthollet's examples of variable composition were all cases of mixtures and that when more than one compound exists between the same elements, the change in the combining ratio is sudden and rather considerable. In other words, when entire mixtures seem to exhibit gradual changes in composition, the effect is actually due to sudden changes by certain parts of their ingredients. The spirited controversy was carried on with brilliance for almost eight years, but with the utmost decorum and good manners on both sides. Berthollet's erroneous idea was refuted and Proust is universally credited with the experimental demonstration of the law of definite or immutable proportions, a law that had previously been axiomatically assumed by most chemists.

It was in line with Berthollet's character that he harbored no hard feelings. Proust was in France attending to family business when the French overran Spain in 1808. His laboratory was pillaged, and he lost not only most of his fortune but also his position.

THE BERTHOLLET STATUE ON THE SHORE OF LAKE ANNECY NEAR HIS BIRTHPLACE, ERECTED IN 1844 BY PUBLIC SUBSCRIPTION. NOTE THE SPHINX AND THE FIGURES OF NAPOLEON, BERTHOLLET, AND MONGE ON THE LOWER PLAQUE.

He was reduced to peddling the few samples of precious minerals he brought with him, offering them to dealers with the plea: "Turn these stones into bread." Berthollet brought Proust's plight to the attention of Napoleon who thought this an excellent chance to promote a new industry. He offered Proust 100,000 francs and a good salary if he would set up and manage a factory for making grape sugar, which Proust had isolated in 1799. Proust declined the offer because of his age and bad health, but especially because he was certain that even though he was a good chemist, he would fail as a chemical manufacturer.

Berthollet's unfortunate error in his controversy with Proust led chemists to throw out the good with the bad, and when they rejected Berthollet's law of variable composition, they also forgot his law of mass action. Furthermore he was in advance of his times. P. Duhem in his "*Introduction à la Mécanique Chimique*" (1893), wrote:

> This excellent book contained some ideas that were so novel for the time at which they were written that Berthollet's con-

MÉMOIRES
DE PHYSIQUE
ET DE CHIMIE,
DE LA SOCIÉTÉ D'ARCUEIL.

TOME PREMIER.

PARIS,

J. J. BERNARD, QUAI DES AUGUSTINS.

M. DCCC. VII.

TITLE PAGE OF THE ARCUEIL MEMOIRS

temporaries did not understand them. Unfortunately, along with concepts which today seem to have been almost prophetic, it contained denials of the law of definite proportions. The broad truths in the "*Essai de Statique Chimique*" were forgotten and only the memory of the errors was preserved. One of the greatest chemists and one of the finest books of the beginning of the century have thus been constantly misjudged.

As previously related, the ideas of mass action, reversible reactions, and chemical equilibrium eventually received adequate attention, and Berthollet's work marks the real beginning of chemical mechanics.

Berthollet received many honors from Napoleon. Upon the return from Egypt he was nominated senator by the first consul. During the Empire he was made Grand Officer of the Legion of Honor, Grand Cross of the Order of Reunion, Titulary of the rich Senatory of Montpellier, Chevalier of the Iron Cross, and Peer of France with the title of Count. The letters patent of this last appointment, signed by Napoleon, were issued at Bayonne on April 26, 1808; the document now is in the museum at Annecy.

All these marks of distinction produced no change in Berthollet's manners. He retained his democratic ideas and was seldom seen at court. His coat of arms gave proof of his innate simplicity.[28] The heraldic shield was divided into four parts. The upper left quarter bore a mirror and serpent (caduceus) to signify his medical degree; the upper right, an ibis, reminiscent of Egypt; the lower right, a pneumatic trough, symbolic of chemistry; and the lower left, a dog, typifying fidelity.

Berthollet had an apartment at No. 18, *Rue d'Enfer*, between the Luxembourg and the *Boulevard Montparnasse;* the site of the house is now covered by the *Boulevard Saint Michel;* however, he greatly preferred his home in the little town of Arcueil, about four miles out of Paris. The house was on the *Rue de la Montagne* (also called *Rue de Carennes*); the street is now the *Rue Berthollet*. His next door neighbor was the illustrious mathematician and astronomer, Laplace (1749–1827). They visited back and forth frequently, exchanging ideas.

Berthollet bought this country home in order to be near Laplace, whom he admired greatly. Davy visited them in 1813. He wrote:

> Berthellot was a most amiable man, even when the friend of Napoleon, always kind, conciliatory, modest, frank, and candid. He had no airs, and many graces. In every way below Laplace in intellectual powers, he appeared superior to him in moral qualities. Berthollet had no appearance of a man of genius, but one could not look on Laplace's face without being convinced that he was a very extraordinary man.

After Berthollet's death, the property was bought by the Benedictines who started a school in the house. About 50 years ago the *Caisse des dépôts et consignations* acquired the property and the house was taken down shortly thereafter. Its site, the present No. 16, is now occupied by the bank building.[29] Although reverence for historical associations can easily degenerate into useless sentimentalism, it is regrettable that no attention was paid to the historical values in this house. The drawing room had a superb ceiling embellished with Egyptian designs. In the garden was a stone table, and sometimes Napoleon sat there to listen to the scientific conversations.

Berthollet built a laboratory in this retreat and encouraged young men to work with him so that he could inculcate in them that same love of science that had dominated his whole life. He always was glad to receive visits, even from those who had vigorously opposed some of his ideas. Scientists from abroad were often his guests.

Sir Charles Blagden (born in 1748) died in Berthollet's house on March 26, 1820. Blagden, who like Berthollet was a physician by profession, did some creditable chemical and physical work. He was

[28] See THIS JOURNAL, **23**, 162 (1946).

[29] The Laplace house has also been removed; the site is now a park. Both of these properties had interesting histories. The Berthollet home had been the residence of the poet, Etienne Jodelle (1532–73), and the poet, Pierre Ronsard (1524–85), lived in the Laplace home.

assistant and amanuensis to Cavendish, who left him $80,000. He became Berthollet's correspondent in the *Académie des Sciences* in 1784. He was elected Secretary of the Royal Society through the influence of Sir Joseph Banks. He spent much time in Paris and became one of Berthollet's intimate friends.

In 1807, Berthollet founded the *Société d'Arcueil*. A record of its proceedings is preserved in the three volumes of its *Mémoires*. The foreword (July 9, 1807) stated:

> A society of several persons who cultivate the different branches of chemistry and physics has been formed with the view of strengthening their individual forces by a union based on mutual esteem and related tastes and acquirements, but avoiding the inconveniences of an association that is too large. It meets every 15 days at Arcueil. The day of the meeting is devoted to repeating new experiments which seem to merit this attention because of their brilliance, or which need to be confirmed, and to perform those that are suggested by some member of the Society, especially those that require special apparatus, or in which the author desires to have some assistants, witnesses, or advisors. All the papers which are to appear in the record of the Society are submitted to discussion; but the author remains entirely free as to his opinions, and he alone will be responsible for them. Each member agrees to read one or more journals and books that are published and which deal with the science that he particularly cultivates. A report of these is given at the meeting.... The one who conceived the plan of forming this association, seeing the end of his career approach, derives great satisfaction in contributing by this plan much more effectually to the progress of the sciences to which he is devoted than he might by any researches which he could still promise himself to continue.

The list of members given in the first volume of the *Mémoires* (1807) comprised Berthollet, his son, Biot, Collet-Descostils, Decandolle, Gay-Lussac, Humboldt, Laplace, and Thénard. Malus had been added when the second volume appeared in 1809. The members in 1817, when the third and last volume was published, were Arago, Berard, C. L. Berthollet, Biot, Chaptal, Decandolle, Dulong, Gay-Lussac, Humboldt, Laplace, Poisson, and Thénard.

The quality of the papers presented before this group was high, and Berthollet was a frequent contributor. Some of the work reported here was outstanding, such as Dulong on nitrogen trichloride and Thénard on esters. Two of the papers were epoch-making. Malus, in his study of the properties of reflected light, discovered polarized light, an achievement that may be regarded as the origin of Pasteur's work on optical activity. The report by Gay-Lussac on the volume relations of reacting gases and their gaseous products had an important part in putting the atomic theory on a firm foundation.[30] Gay-Lussac and von Humboldt became intimate in the Society at Arcueil, and this association eventually led to Gay-Lussac's analyses of air, which in turn resulted in his discovery of the law of combining volumes of gases.

A great tragedy came to Berthollet in 1811. His son, who showed excellent talents in chemistry, started a chemical business. He failed badly and, in despair, committed suicide at Marseilles.[31] Berthollet's own fortune was seriously involved in the bankruptcy, but he made no complaint. Napoleon sent for him and said reproachfully: "M. Berthollet, I always have one hundred thousand crowns at the service of my friends," and this sizable sum (300,000 francs) was given to him at once.

In view of this generous and understanding act, it is hard to explain why Berthollet, in 1814, voted in favor of dethroning the Emperor. Did he place what he believed to be best for the nation above his private feelings of friendship and gratitude? Or was he persuaded by Laplace, who also voted against Napoleon?[32] Napoleon felt Berthollet's defection keenly. "What! my friend Berthollet! Berthollet, on whom I would have relied so much!" During the Hundred Days after Napoleon's return from Elba, Berthollet naturally received no government preferment; however, he went to the Tuileries, soliciting attention, and Napoleon did not have the heart to refuse this small favor.

Berthollet took his seat as peer after the restoration of the Bourbons, but he was feeling his age, and his misfortunes had taken their toll of his health and spirit. Guyton de Morveau died in 1816 and Monge in 1818. Berthollet retired from public affairs more and more, but he did consent to become mayor of Arcueil in 1820. He also gratefully accepted nomination to the Academy of Medicine when it was founded; however, he refused to allow his name to be given the alkaloid that had been isolated from cinchona bark. He wrote in a letter to the discoverers, Pelletier and Caventou, on May 1, 1820:

> I am quite appreciative of the honor you have wished to confer on me by giving my name to the substance that you have discovered, but I think it much more suitable to take its name either from the material that furnishes it or from some of its properties. It was for this reason, that the name "Vauqueline"[33] has not been accepted, and "strychnine" has been substituted in its stead. I therefore beg you to make this change.

Consequently, quinine was not given the name "Bertholline."[34]

In 1822, Berthollet had an attack of fever which left behind it a number of boils. These developed into a large gangrenous ulcer, which probably was cancerous.

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[30] LEMAY, P., *"Berthollet et la Société d'Arcueil,"* *Courrier Médical*, p. 59 (1934).

[31] "Returning to a small room, he locked the door, closed up every chink and crevice which might admit the air, carried writing materials to a table on which he placed a second-watch, and then seated himself before it. He now marked precisely the hour, and lighted a brasier of charcoal beside him. He continued to note down the series of sensations he then experienced in succession, detailing the approach and rapid progress of delirium, until, as time went on, the writing became confused and illegible, and the young victim dropped dead upon the floor." T. THOMSON, *op. cit.*, vol. 2, p. 151.

[32] Laplace lauded Bonaparte extravagantly at the outset and was made Minister of the Interior; however, he showed such incapacity for business affairs that after six weeks, he was removed by the First Consul and replaced by Lucien Bonaparte. Thereafter, Laplace could find no good in Napoleon.

[33] L. A. Vauquelin (1763–1829), a leading chemist of his time, had isolated quinic acid from cinchona bark. When Caventou and Pelletier, in 1818, suggested calling their new alkaloid after him because he was the first to call attention to a toxic plant principle, a committee of the Academy reported "that a revered name should not be applied to a malevolent principle."

[34] LEMAY, P., *"Berthollet et la baptême de la quinine,"* *Courrier Médical*, 1934, p. 877.

BERTHOLLET'S TOMBSTONE IN THE CEMETERY AT ARCUEIL

He suffered for several months with uncommon bravery. As a physician, he followed the inevitable progress of the malady and calmly regarded the slow appoach of death. At length, after a tedious period of suffering in which his equanimity had never once been shaken, he died on November 6, 1822.[35]

His grave is in the cemetery at Arcueil.

The restoration of the Bourbons and the consequent elimination of payments to the favorites of Napoleon had left Berthollet with a greatly reduced income. His widow was in straitened circumstances. She was taken into the home of one of their former servants who kept a tavern, "The Good Faith," in Paris on the *Avenue d'Orleans*. In his will Berthollet left to Gay-Lussac his regalia as Peer of France. This created much talk; however, Gay-Lussac was not raised to this rank until 1839, probably, as Arago reported, because "every morning the great chemist worked with his hands in the laboratory at the Mint, and such labors seemed incompatible with the dignity of a Peer of France."

A bust of Berthollet, facing one of Laplace, graces the entrance to the town hall of Arcueil. These were formerly at other sites in the city, but they had to be moved because they were damaged by thoughtless vandalism several times. The gratitude of men is often short-lived! In 1844 a public subscription under the auspices of Charles Albert, Duke of Savoy, provided funds for a monument on the shores of the Lake of Annecy near the place where Berthollet had been born almost a century before; however, the most lasting monument to this eminent chemist are his books and his more than 80 papers.

[35] THOMSON, T., *op. cit.*, vol. 3, p. 152.

CAN WE AFFORD GOOD EDUCATION?

Our current expenditure now is about 2.5 billion dollars annually for public elementary and secondary education. This amount is 1.5 per cent of America's national income in 1943. In 1940—just prior to our entry into the war—we spent 3 per cent of our income for schools.

Before World War I we devoted more than one-fourth of all tax collections to the support of public elementary and secondary education. Today we are using about 5 per cent of total tax collections.

Between 1939 and 1942 the American people increased their expenditures for alcoholic beverages from 3.4 billion dollars to 5.2 billion dollars; for tobacco, from 1.8 billion dollars to 2.4; for beauty treatments and cosmetics, from one billion dollars to 1.5 billion dollars. Every indication is that the expenditures for these same luxuries rose to even higher levels in 1943, 1944, and 1945.

Comparisons of these figures with expenditures for education give us reason for deep thinking. Obviously a nation with so much money can afford to invest more in the educational futures of all citizens. If civilization is "a race between catastrophe and education," we are giving education far from a reasonable chance. Surely it is as true today as it ever was, "where there is no vision the people perish."

The Thermal Conductivity Method of Gas Analysis

CLARKE C. MINTER

Gow-Mac Instrument Company, Newark, New Jersey

QUANTITATIVE determination of the percentages of the various constituents of a mixture of gases is usually accomplished by performing a chemical analysis which involves a certain number of operations with a gas analysis apparatus. The procedure necessary to determine the percentage of any one constituent consists of measuring a definite volume of the mixture into a gas analysis buret, bringing the gas into contact with a reagent which will react chemically with the particular constituent of the mixture being determined, and, finally, measuring the change in volume after the removal of this constituent. This procedure has to be repeated with different reagents for the removal of each of the other constituents of the mixture until the composition of the mixture is entirely known.

It can be seen from the brief outline above that ordinary gas analysis is a slow and tedious process. Aside from the possible errors due to gas leaks in the apparatus, incomplete reaction between the gaseous constituents and the absorbing reagents, the chief disadvantage of the chemical analysis method is that it is discontinuous. This feature is objectionable in certain industrial operations involving gases and vapors where continuous control is necessary. It would not be possible to control certain processes accurately and efficiently if discontinuous or intermittent chemical analysis were employed.

It is possible to obtain a continuous indication of the composition of a mixture of gases, or of gases and vapors, by means of an apparatus designed to measure and indicate the magnitude of a certain physical property which varies with the percentages of the constituents in the mixture. The property of the gases which is employed is known as the thermal conductivity of the gas, which is a measure of the quantity of heat conducted in unit time between two unit surfaces in the gas when they are unit distance apart and the temperature difference is one degree centigrade. While this definition makes the method sound quite complicated, as a matter of fact, the apparatus used for measuring thermal conductivity is relatively simple in design and inexpensive to build.

In order that the thermal conductivity method of gas analysis may be employed, it is essential that the gases in the mixture possess thermal conductivities of sufficient difference in magnitude to produce a measurable difference in thermal conductivity for a small change in the composition of the mixture. In addition, it is necessary that the thermal conductivity of the mixture vary more or less linearly with composition over the range of concentrations to be analyzed. There are certain binary mixtures, such as air-water, air-ammonia, and air-butane, which exhibit a maximum conductivity; but the ascending and descending portions of the conductivity-composition curves can be used so long as it is definitely known which range of composition is being analyzed. For the most part, however, the thermal conductivity of two-component mixtures, and also multi-component mixtures, will be sufficiently linear with changes in composition to enable simple calibration curves to be used on the indicator scales.

Instead of employing an apparatus which will measure and indicate the absolute thermal conductivity of a gas, it is much simpler to make a direct comparison of the thermal conductivity of the unknown gas with that of a standard or reference gas, the nature of which will vary with conditions. The thermal conductivities of the unknown gases are then measured relative to air, to hydrogen, or to any other suitable standard. By so doing, several instrumental errors are eliminated, particularly those due to changes in temperature of the apparatus. Since the absolute conductivities of the reference gases are known, it is a simple matter to calculate the absolute conductivity of the unknown gas from the relative conductivity, when, and if, absolute values are needed. It is not always a question of having to know the absolute or relative thermal conductiv-

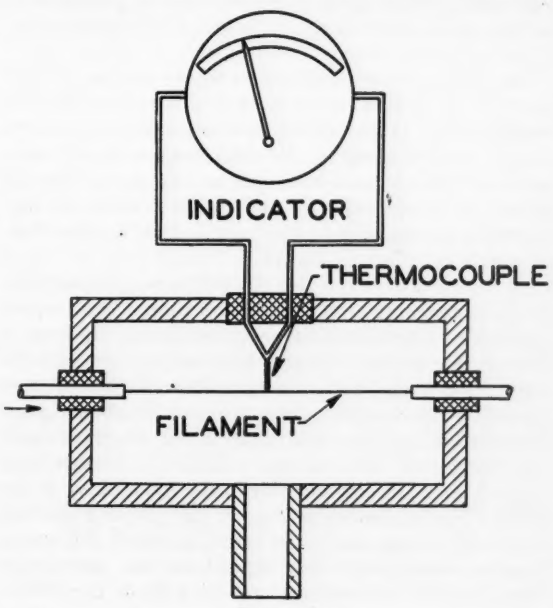

FIGURE 1

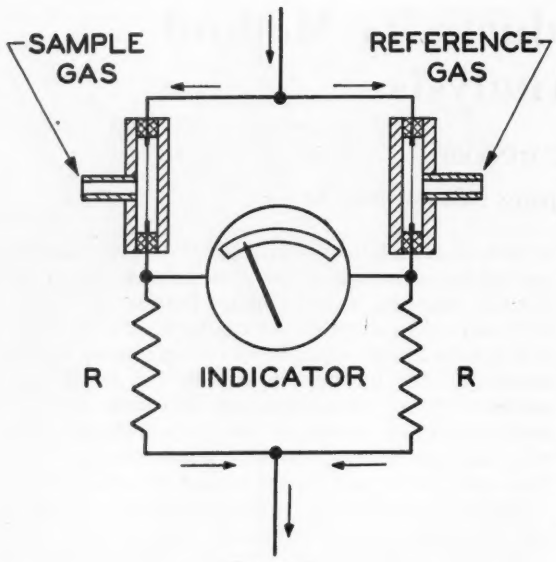

FIGURE 2

ity of the unknown. The only question that is really important is how much change on the indicator can be produced by a given change in the composition of the mixture.

The type of apparatus used in gas analysis by thermal conductivity is very simple in principle and design. Figure 1 shows diagrammatically the fundamental principle of all thermal conductivity apparatus. A fine wire heated by a current is surrounded by a gas which conducts heat from the wire to the walls of the chamber. A fine thermocouple in contact with the hot wire measures its temperature above that of the wall of the chamber, which difference will be inversely proportional to the thermal conductivity of the gas for a given power input to the hot wire.

The design shown in Figure 1 would not be suitable as a practical instrument for gas analysis by thermal conductivity. It has already been mentioned that the thermal conductivity of the unknown gas can be compared with that of a reference gas, usually air; and the difference in temperature of the two hot wires, or filaments, is measured by other means than by the thermocouple as shown in Figure 1.

In Figure 2 we have two similar current-heated filaments in two similar cells, and two similar inert resistances, the four elements being connected to form a Wheatstone bridge. If one cell contains air and the other cell contains a gas having a different thermal conductivity, the two hot wires will not be at the same temperature, and they will not have the same resistance. The bridge will then become unbalanced to an extent depending on the conductivity of the gas relative to the standard or reference gas; or, in the case of a mixture of variable composition, the extent to which the bridge becomes unbalanced will depend on the percentage composition of the mixture, and the scale on the indicator can be calibrated in terms of per cent composition. The Wheatstone bridge is now universally used in thermal conductivity apparatus; and there are usually four sensitive filaments instead of two as in Figure 2, which will double the sensitivity to a given change in composition.

It is not difficult to see that the thermal conductivity method of gas analysis is much easier and simpler to carry out than the method of chemical analysis already described. The feature of continuous indication is also evident, as well as the advantages in process control.

The quantity of heat conducted by a gas varies with the nature of the gas, extending from poorly conducting vapors having only one-fifth the conductivity of air, to hydrogen having seven times the conductivity of air. Gases and vapors of any conductivity between these two extremes can be accurately analyzed by proper selection of the reference gas. The values of the absolute thermal conductivity for a large number of gases and vapors have been determined and can be found by reference to any of numerous handbooks of physical and chemical data.

Most of the applications of the thermal conductivity method so far have been to mixtures containing only two components—such mixtures as carbon dioxide in air, hydrogen in electrolytic oxygen or oxygen in electrolytic hydrogen, acetone vapor in air, air in the helium or hydrogen of balloons and dirigibles, hydrogen in the air of submarines, and so on. For an interesting application of the thermal conductivity method see "A New Technique for Absorption Studies" by Coull, Engel, and Miller (*1*); however, by far the most extensive employment of the thermal conductivity method has been to multi-component mixtures produced by combustion of carbon and hydrogen, principally in internal combustion engines (*2*). In the first use of this application the entire mixture of combustion products, consisting of nitrogen, carbon dioxide, carbon monoxide, and hydrogen, is put through the conductivity apparatus, and its conductivity compared with that of air as standard. Since the purpose of analyzing the combustion products is to be able to estimate the ratio of fuel to air in the combustible mixture, there would be no practical advantage in knowing the detailed composition of the products of combustion as a function of mixture ratio, when a simple linear relation exists between the thermal conductivity and the mixture ratio. Another example is the determination of hydrogen in a multi-component mixture (*3*).

This same technique can be applied to other multi-component mixtures which are produced during industrial operations. Instead of following the variations in the concentration of a single component of a mixture and trying to regulate a process so that a mixture having a given concentration of that particular constituent is produced, it is much simpler to determine the thermal conductivity of the complex mixture when it contains the desired percentage of the given constituent and to control the process under consideration so that it has the desired thermal conductivity, forgetting entirely

about individual constituents of the mixture. There must be many places in process industry in which this technique can be applied to advantage where complex mixtures of gases and vapors are present and have to be analyzed to follow the progress of a process or to regulate the quantities of materials being put into the process. The foregoing remarks do not apply, of course, to experimental research in which complex mixtures of gases and vapors have to be analyzed in detail.

When it is necessary to have such information, the exact composition of a multi-component mixture can be obtained by thermal conductivity methods which will give a continuous indication on several indicators of the concentration of several constituents. To obtain such a result, a thermal conductivity unit for each constituent must be used, each unit with an indicator appropriately calibrated if continuous indication is desired. The procedure is known as the differential method, and consists in comparing the thermal conductivity of a mixture with that of the same mixture after absorption of the constituent to be determined in a suitable absorbing agent. If this is repeated with different absorbents for the various constituents, the mixture can be completely analyzed by means of thermal conductivity; however, if at all possible, it is much simpler to employ the technique described above although some research would doubtless be necessary to establish the relation between the composition and the thermal conductivity of the complex mixtures.

A special application of the thermal conductivity method of gas analysis (*4*) makes it possible to obtain quickly and accurately the carbon-hydrogen ratio in a mixture of volatile hydrocarbons, such as gasoline, while the determination of this ratio by ordinary chemical methods is a slow and difficult process. If hydrocarbons of known composition, such as pure compounds, are used as fuel for a single-cylinder engine, and the carbon dioxide in the exhaust determined when the exhaust has a given conductivity, it will be found that a definite relation exists between the per cent carbon dioxide at that point and the per cent carbon in the hydrocarbon. Once this relation is established, it is necessary only to determine the carbon dioxide at the selected point for the fuel of unknown composition and refer to the graph for the per cent carbon in the fuel.

In Figure 3 is shown a typical modern thermal conductivity unit containing the cell block mounted in a

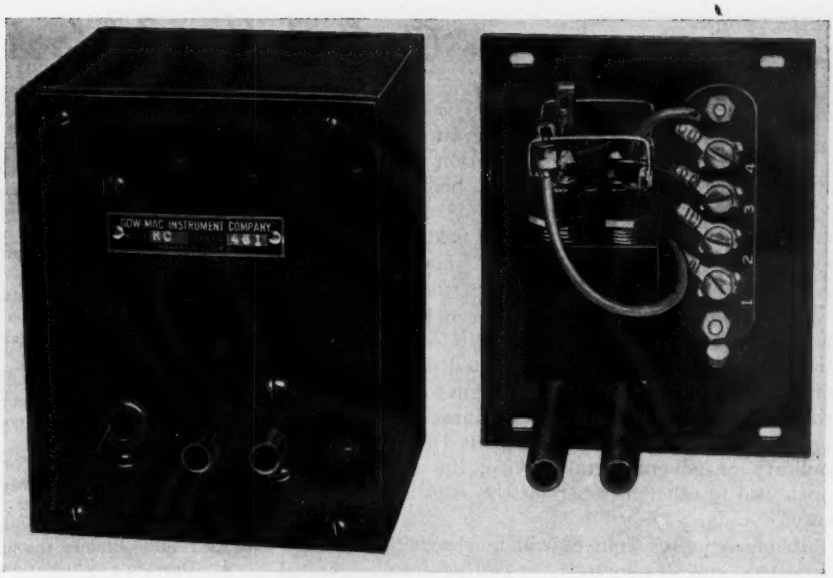

FIGURE 3

suitable housing with the gas inlet and outlet and terminals for connecting the unit to a source of current and to an indicator which can be remotely located. The cell block contains four cells symmetrically spaced. Two of the cells are for the reference gas, usually air, and the other two are for the gas to be analyzed.

In testing, it is possible to have the standard gas dry or saturated with water vapor. In the first case a drying agent must be placed in the gas passages adjacent to the cells containing the reference gas; in the second case a wet wick is used to saturate the gas. The gas to be tested can also be wet or dry, and suitable saturating or drying equipment has to be used in the gas line ahead of the cell unit.

The four filaments in the cell unit shown must be carefully selected and matched for both resistance and temperature coefficient of resistance. A good cell unit should be so well matched that when all four cells contain the same gas, say air, the bridge balance should not change perceptibly for a change of current through the bridge of 10 milliamperes on either side of the normal operating current. Also a good bridge will show no change in balance when the temperature of the block is varied as much as 50°C.

If proper care is taken in making a number of bridges, it is possible to make the bridges so that there is no perceptible difference between them. This is of advantage when making replacements, since all bridges would give the same output for a given difference in conductivity.

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(4) MINTER, C. C., *Nat. Petroleum News*, **25**, 33 (1933).

Out of the Editor's Basket

A PROJECT under consideration by the Ethyl Corporation is typical of what is being done by a number of concerns.

Ethyl field engineers and research laboratory staff members who have been on military leave during the war years will be brought up to date on the corporation's present activities and projected plans by means of a series of refresher courses to begin soon. Although the refresher courses of two weeks' duration are planned primarily for field and technical men who have been in military or governmental service, the series will be open also to other members of the sales and technical service staffs.

Included in the courses will be discussions of new processes and developments resulting from technical advances by the petroleum and automotive industries, a review of Ethyl's wartime services, an outline of current sales and research activities, and discussions of future plans.

As part of a comprehensive program, a series of special training courses for new Ethyl employees, similar in scope to courses given before the war, will be conducted as soon as candidates have been selected from graduates of outstanding engineering colleges and universities to be trained for positions in research, technical service, and sales.

Netherlands Indies

There has just come to us a copy of a pamphlet, "Scientific Institutions, Societies, and Research Workers in the Netherlands Indies." Any who are interested in scientific work in this locality may obtain one from the Editor, *Chronica Botanica*, P. O. Box 151, Waltham 54, Massachusetts.

A Notable Inventor

A pamphlet on the life and achievements of George Westinghouse has been published by the Westinghouse Electric Corporation (306 Fourth Avenue, Pittsburgh, Pennsylvania).

Teaching and Research

In the March, 1946, number of *School Science and Mathematics* is an article entitled "Toward a better science teaching profession" by Lee R. Yothers. The value of research in the training of science teachers has seldom been more clearly shown than here:

RESEARCH

The statement, "we are living in a scientific age," is now an encyclopedic one. Perhaps it would be more descriptive to say, "we are living on the border of an intensive and extensive international scientific research era." There is, therefore, an increasing need for science educators from kindergarten through the university to become the laymen's interpreter of science fundamentals which have been acquired from research specialists. The utilization of this scientific knowledge may be heightened through an understanding and, in addition, a fair degree of skill in using and teaching research techniques. An objective of every science teacher should be to familiarize himself, in the early era of his career, with procedures of research. While advanced research may not always be feasible, certain features of this work may be accomplished by adopting an independent study of many problems of research nature.

In all probability early studies will be of no value to anyone except the teacher. However, information and *experience* secured in this manner, over a period of years, will be followed by better and more useful teaching. Definitely both the teacher and students will gain many advantages from effort put into this work. Among them will be the following:

1. A more meaningful cooperation between research specialists and science teachers.
2. A sympathetic appreciation of the vast amount of time, energy, and money necessary for conducting scientific experimentation.
3. More intelligent interpretation to students and laymen of the results obtained through scientific research.
4. Develop a systematic analysis of problems.
5. Gain an understanding of the methods employed by accomplished research workers.
6. Develop a desire to find real facts.
7. Increase ability to instill the spirit and desire for research into capable students.

Training for Industrial Research

We commend to all our teacher-readers a little article, "Selection and training of students for industrial research," by A. W. Hull, which first appeared in *Science*, **101**, 157–61 (1945), and which was reprinted in the *American Journal of Physics*, **13**, 269 (1945).

Deferment

The following appeared in Bulletin No. 30 of the Office of Scientific Personnel:

SUPPLY AND DEMAND FOR SCIENTIFIC AND ENGINEERING PERSONNEL

A recent meeting of the Committee on Manpower Shortages in the Office of War Mobilization and Reconversion actually listed in its agenda consideration of the advisability of curtailing deferment by canceling deferment for those few college seniors now deferred. Fortunately, the matter was tabled; but it is a good indication that there is no fundamental change in the attitude of Selective Service on the problem of highly trained personnel. There is a naïve confidence in the Government that the present flood of registrations on college campuses will quickly restore our supply of technically trained personnel, and that our supply was greatly enhanced due to the contributions of wartime training other than the regular college work of civilian students during the war. There seems to be an overly optimistic evaluation of the worth of certain wartime training programs and a misunderstanding of the distribution of present enrollments.

Improving Ph.D. Programs

Research training seldom qualifies doctoral candidates for rich personal and social living within the framework of their jobs, according to a report prepared by Dr. E. V. Hollis, senior specialist in the U. S. Office of Education who recently completed a study for the Commission on Teacher Education of the American Council on Education.

Analyzing the records of 22,509 persons who received their Ph.D. degrees between 1930 and 1940, Mr. Hollis found that 65 per cent entered the college teaching field, 20 per cent took jobs in industrial research, 10 per cent found work with the government, and 5 per cent entered pre-collegiate institutions. He found 13 per cent engaged in work unrelated to their training or at jobs requiring no more than undergraduate preparation. He found Doctor of Philosophy holders in such positions as village postmaster, rental agent, village banker, police court judge, and clerical workers.

Insulating Material

A new foam material, produced in Germany under the trade name "Iporka," is reported by the U. S. Naval Technical Mission in Europe to be an excellent light-weight insulating material for temperatures below 50°C. At higher temperatures, shrinkage is said to occur and to limit the practical use of this material.

Present uses for "Iporka" in Germany include insulation for icehouses, cold rooms, dry ice containers, and storage cars. "Iporka" also has potential value for sound insulation, since it reportedly absorbs approximately 50 per cent of sound directed toward it.

The new material is prepared by addition of a water-soluble urea formaldehyde condensation product to a foam prepared by vigorous agitation of a water solution of a foaming agent and phosphoric acid. Following further condensation, the resultant foam is dried and cut into desired shapes and sizes with a knife, saw, or wire. It can also be bored, nailed, or glued.

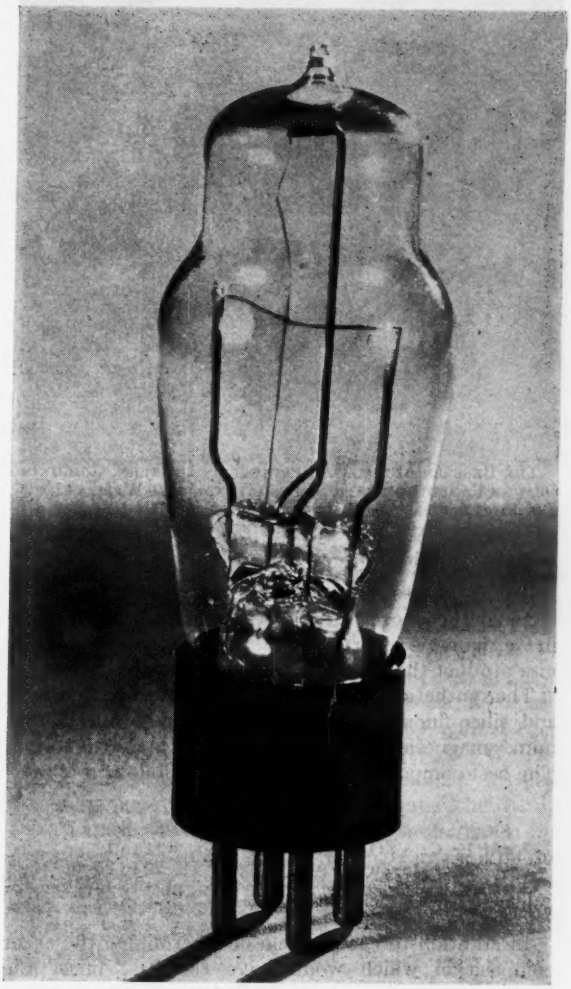
"Iporka" has a density of 0.9 pound per cubic foot and a coefficient of heat conduction of 0.24 British thermal unit per square foot per hour per inch per degree Fahrenheit at 68 degrees mean temperature. In comparison, cork insulation has a density of 10 to 20 pounds per cubic foot. The minimum densities obtained for foams made of other resins, such as polyvinyl chloride and methyl methacrylate, range from 3.5 to 4.0 pounds per cubic foot.

DDT-Wallpaper

DDT insecticide, proved during the war to be one of the most effective means of pest control yet developed, has been incorporated in a new type of ready-pasted cedar closet wallpaper. Moths, ants, flies, mosquitoes, silverfish, and many other insects die shortly after coming into contact with this new wallpaper, which contains five per cent of active DDT insecticide in the top coating. It is nonhazardous to human beings and domestic animals.

New Book

From Rohm & Haas Company (Philadelphia, Pennsylvania) there has just appeared an attractive and nicely bound book, "Chemicals for Industry," which describes many of the products of the company. It is much more than a sales catalog, however, for its beautiful illustrations and interesting descriptions of properties and uses of a variety of substances make it a good addition to one's reference library.

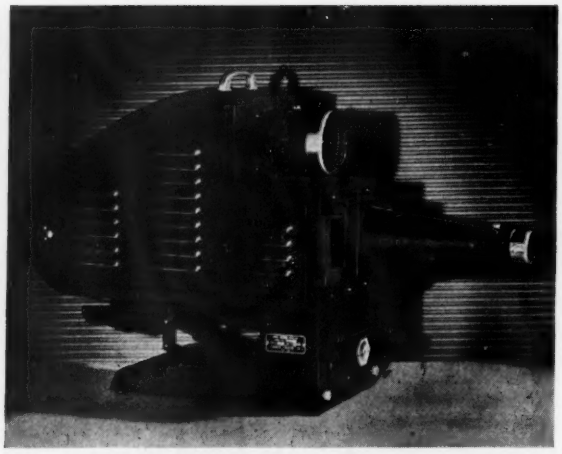


THERMOCOUPLE TUBE

Thermocouple Tube

A tube with a hot junction of a thermocouple element centered on a filament heater and designed to measure gas pressure changes through variations in thermal conductivity of the gas has been announced by Sylvania Electric Products, Inc., Electronics Division, Boston 15, Massachusetts. Used with a microammeter, it will record pressures of 10^{-1} to 10^{-5} millimeters with plus or minus five per cent accuracy. Applications include laboratory use as a pressure gage and leak detector in evacuating apparatus.

Operated in a simple three-volt battery and resistance circuit, it may be sealed directly into evacuating apparatus by means of tubulation provided on top of the bulb. Direct measurement may be made with a 0–250 microammeter which may be calibrated for each gas measured. Maximum accuracy is assured by shielding the equipment from sources of radiant heat and air currents.



THE BESELER MODEL OA2 PROJECTION LANTERN, COMBINING OPAQUE PROJECTION WITH SLIDES, STANDARD AS WELL AS 2 x 2", AND FILM STRIPS.

Synthetic Mica

A new process for production of synthetic mica, perfected in the laboratories of the KWI Ceramics Institute in Germany, is reported by U. S. investigators to result in a product that is as good as natural mica.

The synthetic mica consists of mixed oxides, fluorides, and silico-fluorides containing such metals as aluminum, magnesium, iron, chromium, and vanadium. The best composition is said to be the following:

	Per cent by weight
SiO_2	35 to 39
$(Al, Fe, Cr, V)_2O_3$	11 to 12
(Mg, Fe, Mn, Zn)O	29 to 35
$(Na, K)_2SiF_6$	11 to 13
(Na, K)F	6 to 7

In addition to the problem of determining the exact composition which would give the best mica, the German research workers studied the problem of producing large sheets of mica. The basic means developed for getting larger blocks of mica was to exercise careful control over cooling of the melt, especially in the critical range 1270° to 1230°C., and to introduce a magnetic field at right angles to the vertical axis of the crucible.

Graphite crucibles were used for melting the mix in the laboratory. Electric heating was used experimentally, but either electric heating or a gas-heated furnace would be suitable for commercial production. A magnetic field of 13 gauss intensity was used for crystallization.

Oscillographs

Two convenient catalogs, one dealing with eight of the most popular up-to-date cathode-ray tubes for oscillographic and experimental applications, the other with six oscillographs for precision measurements relating to electricity, mechanics, light, heat, and sound, are now made available for general distribution by Allen B. Du Mont Laboratories, Inc., of Passaic, New Jersey.

Dust Explosions

The dusts of most of the plastics are explosive when in suspension in air, and special precautions are necessary for the avoidance of dust explosions wherever dust is present, either in connection with the manufacture or handling of powders produced from moulding or from grinding or buffing operations. The hazard of plastic dusts has been studied by the National Fire Protection Association, and on their recommendation a Code for the Prevention of Dust Explosions in the Plastics Industry has been adopted by the N.F.P.A. and recently published. This code, prepared by a national committee with the cooperation of the industry, is available from the National Fire Protection Association, 60 Batterymarch St., Boston, Massachusetts, for 25 cents.

Westinghouse Fellowships

Rounding out the transition from war to peacetime industrial research, the Westinghouse Electric Corporation has announced resumption of fellowships to young scientists for work on pure scientific research of their own choosing. Under the plan young scientists, having training equivalent to that represented by a doctor's degree from a recognized university, are chosen from applicants from all sections of the country to carry out research which they themselves outline and initiate. They may be reappointed for a second year if mutually desirable. The fellowship has a value of $3300 a year.

Considered especially important this year are investigations of the fundamentals of ferromagnetism and the properties of semi-conductors. Problems in the fields of nuclear physics, conduction of electricity in gases, dielectrics, thermionics, applied mechanics, and chemical physics are also appropriate.

The discovery of photo-fission, a new type of nuclear fission—briefly the splitting of uranium atoms by high energy rays with a commensurate release of large amounts of energy—was made in 1940 by three fellows appointed in 1938 and reappointed the following year.

Freedom of Learning and Research

The following is reprinted from the *Educator's Dispatch:*

A rift between the military on one side and those educators who insist on freedom of learning and research on the other is threatening to take on serious proportions.

In a little-publicized talk in Washington, National Bureau of Standards director, E. U. Condon, charged the military with "denying to students information essential to understanding." Dr. Condon is a former Westinghouse Electric official, whose present boss, Secretary of Commerce Wallace, also is fighting military control of science. Dr. Condon insists that if what he calls the "military domination of science" continues, "students will get from their professors only a watered-down, Army-approved version of the laws of nature."

The War Department withholds comment on Dr. Condon's charges, but intimates that secrecy of certain facts and research procedures is essential to national security.

Rumblings against the War Department's clamping down on scientists are heard on Capitol Hill, in offices of educational societies, and at the "K" Street offices of the Atomic Information

Committee. Many agree with Dr. Condon's further charges that "Prominent scientists are denied the privilege of traveling abroad. Physicists are not allowed to discuss certain areas of their science with each other, even as between individuals working on closely related phases of the same subject. They can only communicate through official channels, involving censorship of their communications."

Last week in Atlantic City, at least one scientist broke through the alleged censorship by publishing an abstract of a study purportedly suppressed by the Army. Dr. N. J. Curtis of the Tennessee Clinton Laboratories told the American Federation of American Societies for Experimental Biology that the Army had ordered him not to deliver a scientific paper before the Atlantic City meeting A résumé of the study (on the effect of "slow neutrons" on tissues of the body), however, found itself in the printed program circulated among the convening scientists, together with several hundred other abstracts.

Semimicro Methods

From the University of Kentucky comes a short contribution by Simon H. Wender, who has adapted semimicro methods to his use in a special laboratory course for nurses. He is of the opinion that the girls get better results and greater pleasure out of their laboratory work in inorganic, organic, and physiological chemistry when some of it, at least, is on the semimicro scale.

Acetone Synthesis

Large-scale use in Germany of a new synthesis of acetone from acetylene involves passing acetylene and water in the vapor phase over a catalyst of pure zinc oxide. The Germans claim that acetone yields from the process amount to 80 to 90 per cent of the theoretical yield. Though recovery of higher ketones and acetaldehyde would have raised the efficiency of the consumed acetylene, no attempt was made by the Germans to recover these by-products.

Vacuum Keeper

The efficient operation of the many high-vacuum systems used in the atomic bomb project contributed much to its success. This meant that such equipment had to be thoroughly checked for the presence of minute openings through which air carrying foreign substances could seep and thus endanger the process of producing uranium. For this job Westinghouse research scientists developed a fool-proof detector that uses helium gas to ferret out leaks. So sensitive is the device that it can instantly sense the presence of a contaminating substance in proportions as small as one part in several hundred thousand. The exact location of the leak is also shown.

The detector is a special application of the mass spectrometer, an electronic device that weighs and sorts out individual molecules of different gases. It does this by first giving the molecules an electrical charge and then shooting them at high speed down a curved tube. Along the sides of this tube are electromagnets which "guide" the flying molecules so that only those of a particular mass, or weight, pass through an exit slit at the end of a tube and are counted on a special recorder. This means that the presence of a known gas can be promptly detected. Helium is used for leak detection because it is a stable gas that does not react harmfully with other gases or with parts of the system.

THIS DETECTOR, DEVELOPED BY WESTINGHOUSE SCIENTISTS FERRETS OUT SMALL LEAKS IN HIGH-VACUUM SYSTEMS SUCH AS ARE USED IN URANIUM PRODUCTION.

To test a vacuum system, the mass spectrometer is attached to it and pumps started to evacuate the air. Then a thin jet of helium gas is sprayed against each suspected location, or over the entire system. If there is no leak, the detector shows no reading, because normally there is no appreciable amount of helium in the atmosphere and hence there are no molecules of the proper mass to actuate the recorder passing through the spectrometer. Should the detector show a reading when the helium nozzle is held at a certain location, the operator knows instantly that helium is entering some opening in the vessel at that point.

Its star performance in the atomic bomb project marks the helium leak detector as a promising comer in the high-vacuum field, now of greater importance than ever in industry.

Deferment of Students

On September 6, 1945, according to *Russian Research News*, the Gorky State University in Soviet Russia announced the opening of a new radio-physical faculty to train research workers in the field of radio and electronics. By decree of the Council of Peoples Commissars students who enroll in the new school are permitted to transfer from other universities and to defer their call-up for military service.

Contrast this with our own deferment policy for students.

Russian Technical Summary

We have just seen the first number of *Russian Research News*, to be published periodically by the American-Russian Institute. It is intended to be an abstract summary of technical and scientific developments in the U. S. S. R.

Here and There in the Trade Literature[1]

THE conception and construction of the enormous "project" at Oak Ridge, Tennessee, is one of the most interesting stories which has come out of the war. It is told, with many personal touches, in an article entitled "The first 1000 days" in the February number of the *Monsanto Magazine*. In high lighting the article, the editor says: "To the people of Clinton Laboratories the atomic bomb is the infant beginning, not the end, of man's quest for a more perfect way of life."

● Plutonium as a source of energy is something about which we will hear a good deal from now on. As an introduction we suggest you read the article "Petroleum vs. plutonium" in the February number of *The Lamp*. Here is the glimpse given of the future:

Few of us will live to drive atomic automobiles or fly jet planes powered by nuclear energy. When this time arrives, there will still be a petroleum industry, but it may have changed rather remarkably in character. Instead of petroleum's being used primarily for fuel, it will be the raw material for all kinds of organic substances.

Already it sometimes seems a waste to burn hydrocarbon molecules when they can be converted into valuable compounds like synthetic rubber, toluol, polymerized lubricants, plastics, and medicinal substances. The war has emphasized the importance of petroleum as a source substance in organic synthesis. An increase in the availability of atomic energy, together with an increase in the knowledge of the organic chemistry of petroleum, should result in considerable expansion of the chemical utilization of petroleum.

The refinery of the future will be more of a chemical factory than a producer of fuel.

Two other articles in the same number will be worth noticing: "Oil under water" and "Electronics tell how oil pools behave."

● The February *Esso Oilways* leads off with a little sketch of Albert Einstein.

● The whole winter number of *Research Today* is a monograph on the chemistry of the B vitamins. Their structures, syntheses, and properties are dealt with in some detail. The structural flow-sheets of syntheses are especially valuable.

● The following comes from the *Research Viewpoint* (No. 45):

FINISH ALWAYS IN SIGHT

A news article describes a finish for glass which gives it a "dull shine." This article reminds us that for some time we have been marveling at the progress made by research men in the matter of finishes for metals.

Take aluminum, for example. The *Aluminum News-Letter* points out that a short half century ago aluminum had just one finish—Nature's. Today more than a dozen mechanical finishes, plus numerous chemical and electrolytic-oxide and electroplate finishes, reflect the achievements of science in providing a brilliant array of new surface variations for the metal.

And the end is by no means in sight. Not in the least complacent over what has been done to date, the industry's research scientists are still working away at the finish problem—still intent on giving aluminum just about any finish anyone wants it to have, with almost any desired combination of characteristics. Indeed, they seem to be determined to show up Nature as a "piker" when it comes to treating the surface of this gleaming light-weight metal.

For a steadily increasing list of purposes, metals are being sold on a basis of *surface*, rather than solely for their utility characteristics; designers, architects, engineers, manufacturers, and merchants have become definitely surface-conscious. A metal must be economical and efficient for a given purpose; but it must also look well to the eye. And it must retain this attractive appearance throughout its useful life.

Hence, all the research. In fact, since the finish of a metal is always in sight, there is not likely to be any finish to the research on finishes!

● It is no news that auto tires are now enormously better in quality than they were years ago. How developments, both physical and chemical, have brought this about is told in the March *DuPont Magazine*. One side of the story has to do with the production of special qualities of rayon cord, while the other involves many different kinds of substances which serve as antioxidants, peptizing agents, colors, and other compounding agents.

● "Corrosion" is a word derived from the same base as "rodent," both of them having something to do with gnawing; hence the title, "Trapping metal mice," in the January-February *Humble Way*.

● Those interested in vitamin chemistry will find a short account of the fractionation of prothrombin, in the February *What's New*. In the same number is an interesting account of the amino acids and protein hydrolyzates obtained from meat.

● It is a rare number of the *Industrial Bulletin* of Arthur D. Little, Inc., in which there is not at least one item worth reprinting. The March number is no exception, from which we quote the following:

SPITFIRE AT WORK

Sodium, a novelty of high-school chemistry, has become an important chemical. It is a gray metal that can be cut with a knife; it floats on water, and reacts with it to spit fire. In spite of this spectacular characteristic, it can be handled safely industrially, and its extreme reactivity has been found useful in many applications. One of the newest of these is a process recently announced by duPont, largest United States producer of sodium, for the descaling of alloy metals.

In high-temperature metallurgical operations a hard, tightly adherent scale forms on the surface of the metal, and must be removed before subsequent processing. The scale is usually removed electrically or by dissolving it in an acid bath, a process known as pickling. The acid, however, removes some of the base metal, a serious matter with expensive stainless and other alloy steels. In duPont's new sodium hydride process, which avoids this loss, the metal bars or other shapes are dipped into a bath of molten caustic soda maintained at about 700°F. This bath contains from one and a half to two per cent sodium hydride, which is formed in small bottomless containers attached to the inside walls of the tank, by the reaction of hydrogen and sodium metal. The hydrogen is bubbled in at the bottom of the

[1] For the company and address of a magazine cited, see THIS JOURNAL, January, 1946, p. 38.

containers and the sodium is added as bricks at the top. The sodium hydride diffuses through the open bottom of the container into the bath of molten caustic.

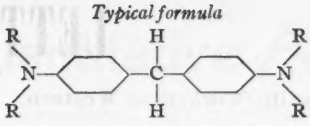
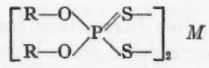
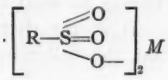
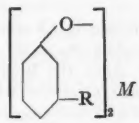
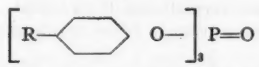
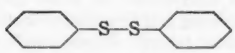
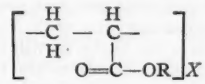
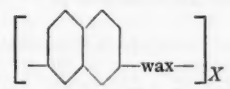
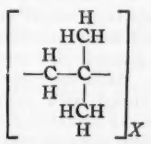
The sodium hydride changes the surface scale to loosely adherent metal, and leaves more caustic soda as the by-product of the reaction. The work, still hot, is then dipped into water; steam formed in this quenching blasts off the loose scale. A final dip into acid to brighten the work may be used, but is not essential. Several commercial installations of this process have already been made and others are now planned.

By far the most important use of sodium metal is in the manufacture of tetraethyl lead, the well-known antiknock ingredient. Although only about 0.04 fluid ounce of tetraethyl lead is used in each gallon of automobile gasoline, the total consumption of sodium in its manufacture totals millions of pounds annually. During the war demand for tetraethyl lead in aviation gasoline curtailed supplies of both sodium and lead for other purposes.

Another use of sodium is in the manufacture of sodium cyanide, which is used in large quantities in citrus fumigation, in metallurgical operations, and in the manufacture of one type of transparent plastic. Sodium peroxide, used for bleaching textiles and groundwood pulp, is also made from sodium. A new process utilizes this bleach in the production of high-quality paper, as well as of cheap newsprint, from ground pulp. Since a wide variety of organic chemicals will react with sodium, the demand for it in the organic field is expected to gain steadily. Many pharmaceuticals, including all the "barbital" series, are derived from sodium. It is an excellent conductor of electricity, and wires with sodium cores covered with copper have reportedly been used in Germany.

Molten sodium is finding increasing use as a heat-transfer medium. The sodium-cooled valve has been called the greatest single step toward improved aircraft engine performance. The hollow interior of a steel valve is partially filled with metallic sodium, which melts when the engine is warm. The sodium, agitated by the valve's movement, carries the heat through the valve stem to the cooling system. Practically all aircraft engines of 300 horsepower or more have sodium-cooled exhaust valves. In America sodium-cooled intake valves have been used in high-output engines and they have been employed, as well, in German and Italian aircraft motors.

Sodium was first used during the latter part of the 19th century in the manufacture of aluminum. It then cost $50 a pound, and in an effort to reduce the cost of aluminum, the Castner process for obtaining sodium by electrolysis of molten salt was developed. Now sodium made by this process costs 15 cents a pound, and world production of it during the war was greater than that of tin.

Type of additive	*Typical formula*	*Function in lubricant*
Antioxidant Organic amine		Increase the resistance of oil to oxidation
Anticorrosive Metal salt of a thiophosphoric acid		Decrease or prevent bearing corrosion
Detergent Metallic sulfonate		Promote general engine cleanliness
or		
Metallic phenolate		
Extreme pressure agent Phosphorus-containing organic compound		Impart high load carrying properties to a lubricant
or Sulfur-containing organic compound		
Pour Depressant High molecular weight polymer		Reduce the pour point of an oil so that it will flow freely at reduced temperatures
or Wax naphthalene condensation product		
Viscosity Index Improver High molecular weight resin		Improve the viscosity-temperature relationship of lubricants

Note: In the above formulas, the following symbols are used:

(1) M = a metal
(2) R = an organic group composed of hydrogen and carbon
(3) X = indicates a number of like molecules condensed together to form a resin-like material
(4) wax = high molecular weight paraffinic hydrocarbon

(*Courtesy of the Texas Company*)

● The improvement of lubricating oils is largely the result of various "additives" which are used in the oil to improve various properties. The above table of Oil Additives, their composition, and uses, is taken from the January *Lubrication*.

"Especially in the natural sciences is it the case that the temptation to early and intense specialization has produced a specialist capable of training other specialists, but ill-adapted to educating youth between 17 and 22."—Ex-president Nielson of Smith College

LETTERS

Relief Packages for Scientific Workers in Western Europe

Several of us have recently often been asked for information about the needs of our colleagues in Western Europe, about the most suitable things to send them, the best way to send these, etc. It seems therefore that it may be useful to broadcast the following information:

(1) There is still a serious shortage of food in all countries of Western Europe which have been occupied by the Axis. Though conditions have improved considerably since the liberation of most of these countries, the calories and vitamins which our colleagues and their families receive and will continue to receive for quite some time in the future are very often still inadequate, and, moreover, food is nearly always given in forms which are dreadfully monotonous.

(2) Scientists in North America who desire to assist their colleagues in Western Europe by sending relief packages should not hesitate to do so, and in the near future. If one has had dealings in the past with an outstanding colleague, one should most positively not be afraid to embarrass him with a gift package. If he does not need it, which is not likely, he will turn all or part of the contents over to one of his associates who may need it more. Packages can also be sent addressed to: "The Staff, . . . Laboratory, University of . . ."

(3) It is advisable to use the folding boxes sold at Woolworth's and similar stores for sending packages to men in the armed forces serving overseas (size about 8 × 12 × 25.5 inches). Experience has shown that these comparatively small boxes go through much quicker and stand up much better in transit than larger boxes. Fill boxes as tightly as possible and wrap each article in kraft (better than newspaper). After the box has been filled and small openings have been closed with such useful things as matches, pins, adhesive tape, razor blades (all wrapped in kraft), it is best to close the boxes with gummed tape. Now wrap the entire box in strong kraft. It is well to put an address directly on the box and one outside on the package. Close with twine (not tape), and tighten well. Only articles which are dry or have been packed in well-closed tins should be sent. Glass jars should never be sent.

Cigarettes (unless already wrapped in cellophane), soap, tea, etc., should be wrapped first in wax paper and then in kraft.

(4) Though it is not possible to give iron-clad rules concerning the things most needed and appreciated, it is safe to assume that the following things will be particularly welcome: Canned meat, canned vegetable fats, canned butter, canned peanut butter, sweetened cocoa (much better than unsweetened cocoa), tea (takes less space than coffee), coffee (now again available in tins), soap (toilet soap or Ivory, scentless), tooth brushes, tooth powder (less risky than tooth paste), razor blades, shaving cream (sticks), needles, safety pins, pins, yarn, thread, shoe soles, shoe laces, elastic (very much needed!), vaseline, matches (wrap in kraft and use to fill small spaces in packages), etc. Dried fruits such as raisins, prunes, figs, and dates are always welcome, as well as hard candy (safer to send than chocolate).

Cigarettes, and cigarettes, and more cigarettes are in many cases more welcome than anything else; they are still often used for unbelievable exchanges for goods or services. Some colleagues prefer tobacco (now again available in tins) or cigars (should be individually wrapped in cellophane).

Colleagues with children will appreciate milk powder, seedless raisins, and an occasional toy.

(5) Postal Regulations permit the sending of one package a week to one addressee. Packages should be clearly marked: "Gift Limited Value."

For the following countries the limit of weight per package is now 11 pounds, the rate of postage 14 cents per pound, and Post Office forms 2966 and 2922 must be filled out and attached to the package: *Norway, Denmark, Finland.*

Poland: The limit is 11 lb., 14¢ a lb.; forms needed, no. 2966 (two copies) and 2922.

Netherlands: The limit is 11 lb., 14¢ a lb.; forms needed, no. 2972 and 2922.

Netherlands Indies: Small packages cannot be sent to the Netherlands Indies, but small cases can be shipped via Messrs. Funch, Edye and Company, Inc., 25 Broadway, New York 4, N. Y., from whom further particulars may be obtained.

Belgium: The limit is 11 lb., 14¢ a lb.; forms needed, no. 2966 (two copies), 2972, and 2922.

France: The limit is 11 lb., 14¢ a lb.; forms needed, no. 2966, 2967, 2972, and 2922.

Italy and *Greece:* The limit is 11 lb., 14¢ a lb.; forms needed, no. 2966, 2972, and 2922.

Yugoslavia: The limit is 11 lb., $1.83 for 11 lb.; forms needed, no. 2966, and 2922.

Czechoslovakia: The limit is 11 lb., $1.70 for 11 lb.; forms needed, no. 2966 and 2922.

England: The food situation in England (11 lb., 14¢ a lb.; forms needed, no. 2966 and 2922) has not been too good lately; in some ways it is worse than it was during the war years. Rationing is said to function smoothly and honestly, but the diet is limited and dull. Conditions are not in any way as bad as they are in most countries of Western Europe and packages should chiefly be sent to colleagues with whom one has had relations for a longer time.

There are a number of firms which make up gift packages for shipping to the countries overseas. They are often in a position to send such things as butter in tins, which an individual cannot easily obtain. A most reliable firm is Fraser, Morris and Company, 119 West 57th Street, New York 19, N. Y., which will send a price list upon request. The Universal Tobacco Company specializes in sending cigarettes, cigars, and tobacco overseas (276 Fifth Avenue, New York 1, N. Y.).

(6) After sending a first gift package, one may enquire if the colleague to whom it has been sent does not have any special needs. Many are desperately in need of things which are easily and cheaply available in the U.S.A., such as slides, cover glasses, certain stains, one or two recent books, rubbers for a child, a hot water bottle for an aged member of the family, some woolen underwear, etc. Medicines are now mostly available in sufficient quantities. Letters received from colleagues to whom gift packages have been sent should be considered as personal communications, and should never be published in full without the writer's consent.

(7) The governments of most of the countries of Western Europe have been acquiring scientific periodicals and also often books published during the war years in the Americas and the United Kingdom. This literature is now being forwarded and will be distributed in due time among the largest libraries. All this is, of course, only a drop in the bucket. Many colleagues are in great need of literature. In most cases they can send older books in exchange or they will be able to pay for books sent within a year or so.

Publishers and managers of scientific periodicals should be liberal in allowing their former subscribers one or two years' credit during the years of the early reconstruction period in Western Europe. When the Nazis left, the financial structure of these countries was in a deplorable state.

But not only scientific literature is needed. "Pocket books" of the better kind can easily be included in gift packages. A few numbers of *Time*, *Life*, or *Newsweek* will find many grateful readers, and a gift subscription to one of these magazines will be very welcome.

FRANS VERDOORN

Chronica Botanica
WALTHAM, MASSACHUSETTS

A Navy V-12 Course in Quantitative Analysis

GEORGE W. BENNETT
Bethany College
Bethany, West Virginia

DURING the War many of the colleges had to alter their traditional presentations of quantitative analysis in order to accommodate themselves to the Navy V-12 or the Army ASTP programs, and new sequences were arranged to meet the emergency.[1] This branch of chemistry allows many variations in organization and sequence of topics, and this flexibility has prompted instructors and authors of textbooks in the subject to follow various routes to reach the same final objectives.[2] Traditionally the laboratory part of quantitative analysis falls into nearly equal divisions of gravimetric and volumetric procedures. Discussion of topics in class has been arranged to parallel or precede similar work in the laboratory. In former years gravimetric methods usually preceded volumetric methods, but after the first World War many instructors reversed this sequence. More recently there has been a tendency to avoid the traditional division in favor of a unified course in which both gravimetric and volumetric methods are used as needed to illustrate topics developed in the textbook. The present paper describes still another sequence of topics.

In this college it was necessary to care for three groups of people, the Navy V-12 group which required one semester on a strict time schedule, a group of premedical students on accelerated programs, and a much smaller group of professional chemistry majors on the standard program recommended by the American Chemical Society. Due to staff limitations the three groups had to be taught concurrently. The Navy groups, moreover, were replaced at the end of each semester, while the civilian groups carried the subject for two semesters. Civilians wished to enter the course in any semester in order not to lose time on the accelerated program. The Navy specified that the one-semester course must include elements of both gravimetric and volumetric methods. The time allowed for the course was two lecture-recitation periods and two three-hour laboratory periods for 16 weeks in each semester. With these several factors and limitations in mind, the following program was designed as an emergency measure.

Instead of the customary shift from gravimetric to volumetric or vice versa at the end of the first semester, this shift was introduced in the middle of both semesters of the year course. The first semester began with simple gravimetric methods, and from mid-semester to its end, volumetric methods were employed. These determinations involved neutralizations and saturation methods. Volumetric methods, this time redox procedures, were continued into the first half of the second semester, whereupon another shift was made to gravimetric methods. This group of determinations involved a somewhat more advanced type of gravimetric procedure. Students were admitted to the course at the beginning of any semester, and they might take only one semester or both semesters in either order. Such a course is neither very difficult to administer nor without its problems. Before enumerating the problems, it seems desirable to give a summary of the laboratory work done in each of the semi-semesters. Class instruction, as usual, preceded all of the laboratory units.

The first semi-semester began with instruction in weighing and the care of the balance. There followed gravimetric determinations of sulfur, chlorine, magnesium, calcium, and nickel. The volumetric work in the second semi-semester included the preparation and standardization of solutions of hydrochloric acid, sodium hydroxide, and primary reference sodium carbonate, also determinations of soda ash, potassium acid phthalate, and vinegar (or alkalinity of wood ashes). The saturation methods included preparation and standardization of sodium chloride, silver nitrate, and potassium thiocyanate solutions. With these solutions determinations of halogens were made by the Mohr, Volhard, and Fajan's methods. There were, then, five gravimetric and five volumetric determinations in the first semester.

In the third semi-semester titrations were continued by means of the following redox procedures: Preparation and standardization of potassium permanganate solution, and by means of it determination of an oxalate and of antimony in tartar emetic; preparation of potassium dichromate solution and with it the determination of iron in an ore; preparation of sodium thiosulfate solution standardized against the dichromate; preparation of an iodine solution standardized against arsenious oxide; determination of copper in an oxide, of arsenic in a Fowler's solution, of iodine in tincture of iodine.

In the fourth semi-semester gravimetric work involved the following determinations: Aluminum and the care and use of platinum crucibles, zinc as the salt of mercuritetrathiocyanato ion to illustrate the use of complex ions, tin and lead in a brass to illustrate separations, and silica in a soluble silicate. There were again five gravimetric determinations and five volumetric determinations. In all of the volumetric work student standardizations were checked by having the students analyze semi-unknowns. These are solutions which everyone runs; all analyses must concur, and failure to do so indicates a need for restandardization. The semi-unknowns included acids, bases, Mohr's salt, iodates, and the tincture of iodine. It will be noted that the laboratory work included no calibrations either of weights or vessels. We concur with others that it

[1] FRIZZELL, L. D., THIS JOURNAL, 22, 248–9 (1945).
[2] VAN PEURSEM, R. L., *ibid.*, 21, 252–3 (1944).

is possible to use up too much laboratory time in weighing in the beginning course.[3]

The only problems that arose in the plan here outlined were experienced by the student who began the course in its second semester. The instructor had to give these students extra instruction in weighing and in volumetric techniques in order to enable them to catch up with the remainder of the class. When the carry-over of first semester students was small compared with the influx of beginning students, the former had some free time on their hands for two weeks. After that time the schedule functioned smoothly.

In the classroom at the beginning of the second semester everyone started off on an equal basis, except that the first semester students had had experience with volumetric calculations which the beginners lacked. Here again, the instructor had to meet these people extra time to bring them to the level of the carry-overs. Again, when the carry-overs were relatively few, they had a little free time until both groups were brought to the same pace. Our experience was, however, that instruction given the beginning students in class work was a most valuable review for the carry-over students. The military time schedule of the V-12 students necessitated strict attention to details, and the prewar (and doubtless, postwar) practice of the slow worker's remaining in the laboratory until dinner time was not possible in their case. In order to speed the program we used some of the suggestions of Damerell and Booth[3] by using some of the unknowns in solution; but instead of calculating percentages, our students reported the total weight of the constituent under analysis which had been issued to him in his 250-ml. measuring flask, thus obviating the necessity of knowing densities of the unknowns issued in solution.

A student on the program outlined in this paper did all of his volumetric work consecutively, flanked on both ends by gravimetric work, or else he had all of the gravimetric work in a continuous unit (the more difficult techniques coming first) with the volumetric work divided. No particular difficulties arose in presenting the class work parallel to, or in advance of, the laboratory operations. It is possible that our experience with this war emergency course might suggest other variations in quantitative analysis instruction for use in peacetime. For example, if returning veterans wish to resume their studies at the beginning of any semester, the course here outlined permits such a program with ease. And again, when a one-semester course must be given concurrently with a full year course, there is much worthy of study in this four semi-semester arrangement of quantitative analysis.

[3] DAMERELL, V. R., AND H. S. BOOTH, *ibid.*, **21**, 178–9, 206 (1944).

Errata: Chemical Russian, Self-taught

Because of certain difficulties with the Russian language, there are a number of misprints in the articles "Chemical Russian, Self-taught: Part II, The Vocabulary Problem; Part III, Russian Inorganic Chemical Nomenclature" by James W. Perry (THIS JOURNAL, **23**, 22–7, 116–22 (1946)). The corrections noted below should be called to the reader's attention without delay so as to minimize the possibilities of confusion.

PART II, THE VOCABULARY PROBLEM

Page 23, 2nd column, 3rd paragraph, fourth sentence.

Russian "кв," "ав," and "ев" (or "эв") usually correspond . . .

Page 23, 2nd column, 3rd table.

эвтектика	eutectic (noun)
эквивалентный	equivalent (adj.)
эфир	ether or ester

PART III, RUSSIAN INORGANIC CHEMICAL NOMENCLATURE

Page 116, 2nd column, 3rd table.

селен Se

Page 117, 1st column, sub-head (6).

In the example listed above the nouns недокись, закись, окись, перекись, and двуокись are all in the nominative singular . . .

Page 117, 1st column, 2nd list.

Calcium bromide is $CaBr_2$, not $CaBr_3$

On page 118, 1st column.

кислота is misspelled several times as кисдота

Page 118, 1st column.

пиро—фосфорная кислота	$H_4P_2O_7$
моноперхромовая кислота	$HCrO_5$

Page 119, 1st column, 3rd table.

углевод carbohydrate

Page 119, 2nd column, 3rd table.

ортоалюминат натрия Na_3AlO_3

Page 120, 1st column, 3rd table.

цианистый водород синеродоводород	HCN
цианистоводородная кислота	hydrocyanic acid

Page 120, 1st column, footnote 8.

хлористоводородная кислота

Page 120, 2nd column, 3rd table.

аммиачный компрессор ammonia compressor

Page 120, 2nd column, 4th table.

азотистоводородная кислота азотоводородная кислота	HN_3

Page 120, 2nd column, 6th table.

NaH_2PO_4 (not NaH_2PO)

Page 121, 1st column, 5th table, last two salts.

Na_3SbS_3
Na_2SnS_3

Page 122, table of trivial names.

киноварь
рвотный камень

HIGH-SCHOOL CHEMISTRY

Youthful Faradays

CHARLES H. STONE

Vermont Junior College, Montpelier, Vermont

ANY teacher of secondary-school chemistry recognizes the fact that pupils' work in the laboratory is very largely a series of verifications of facts already set forth in the textbook. Fred prepares hydrogen; but he already knows that hydrogen is a colorless gas, insoluble in water, and readily combustible. Frieda sets up the apparatus for preparing ammonia, but the book has already told her that ammonia is a colorless gas with a pungent odor, extremely soluble in water. In all cases the pupil is simply a verifier; he is rarely in the role of a discoverer. Along with his experimental work there is always the acquirement of certain manipulative skills of value in all later work, but this does not alter the role in which the pupil acts.

Now it is not to be expected that the young student is going to discover any fact not known already to the teacher or to the more advanced worker, but there are dozens of little problems, the answers to which are not known to the beginner, not set forth in the text or manual, which can be easily solved by simple experiment combined with observation and reasoning. In this work the pupil becomes a discoverer. His finding may not be as revolutionary as that of the production of the first aniline dye or the development of penicillin; but to the young pupil, it is a real discovery, for it reveals through his own effort some fact which he did not know previously.

For some weeks the writer has been directing the efforts of a group of beginners along the lines indicated above. Wherever possible, a little problem was placed before each student with instructions to go ahead and find the answer to the proposition offered. Some of these little problems are set forth below. It will be noted that the topic suggested is not proposed in the text, and no answer is to be found in either text or manual.

1. Priestley showed that mercuric oxide is decomposed by heat into the metal and oxygen. Do other simple oxides—PbO, CuO, ZnO, etc.—also yield the metal and oxygen when heated?

2. The book says that manganese dioxide is a catalyst when used with potassium chlorate in the preparation of oxygen. Prove it.

3. Manganese dioxide has what formula? Do other compounds with similar formulas also act as catalysts with potassium chlorate?

4. Do other chlorates—$Ba(ClO_3)_2$, $Ca(ClO_3)_2$, $NaClO_3$—also yield oxygen when heated?

5. The text recommends zinc or iron as suitable to use with dilute hydrochloric or sulfuric acid in the preparation of hydrogen. Does the acid drive the hydrogen out of the metal? How do you know this?

6. Can other metals—sodium (minute bit in presence of teacher), mercury, magnesium, copper, tin, aluminum—be used to prepare hydrogen? Is there any difference in their action toward dilute hydrochloric acid?

7. Drop a dime into 5 cc. of conc. HCl in a small beaker. Observe five minutes. What has happened? Why?

8. Locate the metals in (6) above in the displacement series. On this basis, how do you account for the difference in their reactions with acids?

9. Lead stands above hydrogen in the displacement series. How does it react with hot dilute sulfuric acid? Why?

10. Following directions, make a supersaturated solution of sodium acetate and let stand, corked, until cold. Feel the tube. Drop in a tiny bit of the original solid solute. Watch. When done, feel the tube. From where did the heat come as the liquid "froze?"

11. Certain colored crystallized salts contain water of crystallization. Heat gently about 2 grams of the following powdered salts: Crystallized copper sulfate, copper chloride, cobalt chloride. What happens? Why the color change? What would happen if water were restored to each of these anhydrous substances? Place a pinch of anhydrous copper sulfate on the palm of your hand and add ONE drop of cold water. What happens? Explain each set of results noted.

12. To 5 cc. of fresh hydrogen peroxide (3 per cent) add 5 cc. of water, a few drops of dilute hydrochloric acid, and some potassium dichromate solution. The result is a test for hydrogen peroxide.

13. See if you can prepare hydrogen peroxide by using barium peroxide and cold dilute hydrochloric acid. How can you prove if you succeeded?

14. Ammonia is prepared according to the text by heating a mixture of slaked lime and ammonium chloride. Write the equation. Using a wet pestle, grind in a mortar about one gram each of ammonium sulfate and solid sodium hydroxide. Is ammonia formed? Repeat using ammonium oxalate and potassium hydroxide (solid). Repeat using ammonium nitrate and barium hydroxide. Repeat using ammonium acetate and calcium hydroxide. Results in each case? If you had six ammonium salts and four bases, by how many combinations could you prepare ammonia? Why does the book recommend ammonium chloride and slaked lime?

15. Into 5 cc. of alcoholic phenolphthalein and 5 cc. of water, drop a pinch of calcium carbonate (precipi-

tated chalk). Results? In a dry evaporating dish heat strongly about one gram of the same powder, using a Bunsen burner below it and playing the flame of another Bunsen burner over the material. After one minute of highest heat, let cool. When cool, drop a pinch of the material into the tube first used. Results? What must have happened? Write an explanation.

16. Heat separately 5 g. each of the carbonates of lead, copper, cadmium, nickel, and cobalt. What happens in each case? Make a general statement.

17. Carbon dioxide is prepared how? Treat various carbonates with acid. Make a general conclusion.

18. Will dilute sulfuric acid act well with marble chips? Why?

19. Manganese dioxide used with hydrochloric acid yields chlorine. Why? Will other dioxides also act that way—PbO_2, BaO_2, SiO_2, SnO_2?

20. What happens when a pinch of potassium permanganate, potassium dichromate, or potassium chlorate is added to 5 cc. of warm hydrochloric acid? Note the odor. Make a general statement.

21. A cylinder of wood charcoal, three-quarters of an inch long and of diameter such that it will slide easily inside a test tube, is pushed up into a tube full of ammonia gas, and the tube is stood in a small beaker of mercury. Why does the mercury rise in the tube? Carefully remove the charcoal and smell it. Conclusions?

22. What is the sum of the valences in $CuSO_4$, KNO_3, $Pb(NO_3)_2$?

23. Red lead has the formula, Pb_3O_4. The four oxygen atoms have a total valence of -8. The three Pb atoms must have a valence of $+8$. This figures $^8/_3$ for the valence of each lead atom; but there is no such valence. How can you explain the true valence?

It would be easy to add many other items to the above. It was interesting to note the reactions of the various pupils to the problems put before them. Here was something new in laboratory work. No longer were they simply verifiers; they were discoverers. Accustomed simply to proving the truth of statements in the text, knowing beforehand what was coming, they were now required to find out the answer to the problem when that answer was not known. For the first time they were asked to become explorers into a new area of knowledge. And, so, like their famous predecessor, these youthful Faradays went to the work with a new idea, a new purpose.

Some individual reactions may be of interest. Dan was surprised when his home-made gun-cotton, laid on his palm and ignited, burned so rapidly that the heat of combustion was scarcely felt. Jane found that the various-colored carbonates of lead, copper, cadmium, cobalt, and nickel, when heated, gave oxides of different colors than the original material; and, since the product was the same in all cases, concluded that this type of reaction must be general. Monty discovered that the hydrated copper salts, when moderately heated, produced anhydrous products of different color than the original, and concluded that water accounted for the difference. Virginia discovered that malachite ore, crushed and leached with nitric acid, the filtrate evaporated to dryness and strongly heated and reduced with illuminating gas, gave copper. Conrad was little intrigued by the perfunctory project of etching his initials on a small rectangle of glass, but the idea of producing a 7 × 9-inch etching of a line drawing chosen from fifty in a book—well, that *was* something! Bill took pleasure in preparing Prussian blue, chrome yellow, and brown lead pigments. And so on with others.

When each little investigation was finished, it was suggested that the pupil put up samples of "before" and "after" in small vials or tubes, tightly stoppered, neatly labeled, assembled in some pleasing form, and accompanied by a little booklet telling the story of the experiment.

It seems to the writer that our various laboratory manuals might be improved by the addition at appropriate points of simple experiments, the answers of which are not known to the student but may be discovered by simple experimentation; the transition from verifier to discoverer will prove to be an interesting experience for the pupil.

POOR FISH . . .

In the forthcoming underwater tests of the nucleonic (atomic) bomb, a huge number of fish will be killed, says an announcement from the Army. Fish, of course, are notoriously rugged individualists; they have no spirit of cooperation whatever.

It occurs to us that if each fish would be willing to give up a little of that rugged individualism in order to form a sort of protective organization for the common good, a lot of lives might be saved. Not that they could prevent the bomb from going off, but at least they'd be able to face the situation together and pass the word around, and possibly arrange to be somewhere else at the time of the explosion.

But, as we say, fish just won't cooperate with one another, and so a lot of them are going to be blown to bits in a couple of months.

Poor fish . . .

Faraday and the Radio Engineer

—an Imaginary Interview

R. H. WRIGHT

University of New Brunswick
Fredericton, New Brunswick

Announcer: "Ladies and Gentlemen, this afternoon one of our engineers here in the broadcasting station had an unusual visitor. Quite by accident, there was a recording outfit switched on and we are fortunate in being able to bring you this record of the conversation."

Engineer: "Two-O-four, two-O-five, call it two-O-four and a half. . ."

Faraday: "Excuse my interrupting. . . ."

Engineer: "Half a sec. Two-O-four point five. Oh, excuse me, sir; what can I do for you?"

Faraday: "I came in to look about, but I very much fear I have lost my way."

Engineer: "Yeah, I guess it's easy to get lost in this place. I got lost myself at first too."

Faraday: "Would it be an imposition for you to tell me something of your work? What, for example, is this instrument?"

Engineer: "Sure. This thing I'm testing is a two hundred micromicrofarad condenser out of an i-f-choke. ."

Faraday: "A two hundred what?"

Engineer: "Two hundred micromicrofarads. Do you know much about electricity?"

Faraday: "A little, a little. I am interested in that word, 'micromicrofarad.' Can you tell we where it came from?"

Engineer: "Oh, that. It's named after Michael Faraday."

Faraday: "And who, pray, was he?"

Engineer: "I guess he was the greatest British scientist since Sir Isaac Newton, and one of the greatest there ever was anywhere."

Faraday: "This is too flattering. . ."

Engineer: "No it's not! Look. Between 1820 and 1850 that man managed to lay the foundation for the whole modern electrical industry. He made the first electric motor, the first electric generator, he made the discovery that led finally to the radio, and a lot more. He did some chemical stuff too, but I don't know much about that. Anyway, I guess Michael Faraday's what you'd call an 'immortal.' "

Faraday: "Upon my word, sir, I'm truly embarrassed."

Engineer: "What's the matter?"

Faraday: "I am Michael Faraday."

Engineer: "But he's been dead 80 years."

Faraday: "A moment ago you did me the honor of saying I was immortal."

Engineer: "Yes, but . . ."

Faraday: "Then say no more about it. Just now you mentioned the electrical *industry*. What is that exactly? In my time there was an electrical science but no electrical industry."

Engineer: "Well, it's got all kinds of branches. First, I suppose, there's the power industry. I don't know what the figure is now, but a few years ago, just in Canada alone, we were generating over ten million kilowatts."

Faraday: "Kilowatts? I presume that would be named from James Watt. He died while I was still a young man so I didn't meet him—till later. But you were saying?"

Engineer: "This country's full of power of one kind or another. I think it works out at something like ten horsepower per head of the population."

Faraday: "Now that is something that pleases me mightily. I remember France being a very powerful country in Bonaparte's time, but no one ever thought of reckoning the power at so much per head."

Engineer: "I don't think you've quite followed me, sir. The kind of power I'm talking about is mechanical power—the kind we use to describe the performance of steam engines and electrical machinery."

Faraday: "I see .... Yes, I remember now, a few years before I retired I heard Mr. J. P. Joule read a paper to the Royal Society along that line. I confess I did not understand it as fully as I might have."

Engineer: "Come to think if it, I don't believe the idea of that kind of power *was* properly understood until your electrical discoveries and Watt's steam engine made it a live issue."

Faraday: (Chuckling) "I remember one day young Mr. Gladstone (Mr. William Ewart Gladstone—you've heard of him?) came to see some of my electrical experiments. After I had shown him them, he wanted to know whether they would ever be of any practical use. Knowing he was bent on a political career, I told him that one day he would be able to tax them."

Engineer: "You hit the nail on the head that time. The electrical industry is one of the richest there is."

Faraday: "Did I understand you to say just now that all this mechanical power is divided up among the population?"

Engineer: "Well, not altogether. Some of the power plants are publicly owned, if that's what you mean, but a good many belong to private corporations."

Faraday: "What becomes of the power then?"

Engineer: "Some of it's used for running industries, and a good deal of it is used for electric lights—like that one up there. Here, I'll turn it on."

Faraday: "Wonderful!"

Engineer: "And then there are things like vacuum cleaners and electric refrigerators and washing machines and so on."

Faraday: "You bewilder me. These things you mention—do I understand you to say they are all in some way connected with the electric force?"

Engineer: "That's right."

Faraday: "And everyone has all these things? So many kilowatts of them per head?"

Engineer: "Not exactly. In the cities most people have electric light, but not so many have the other things. In the country it's not nearly so good. I forget what percentage of our farms have electric power, but taking the country as a whole I'd say most of them don't."

Faraday: "How is that?"

Engineer: "They used to say it would cost too much money, but the way things have been done in this war, people just laugh if you tell them that now. We've got all kinds of plans for reconstruction and development now."

Faraday: "Development is something I know little about. During my lifetime, it was always my desire to discover new facts and relations rather than to increase the force of things already known. I assured myself that the new facts I discovered would find their full development in due time."

Engineer: "Well, we haven't done a bad job of developing them technically. Where we've fallen down so far is in not making it possible for enough people to use them—or in not using them the right way."

Faraday: "What do you mean by that?"

Engineer: "Here's one way, Mr. Faraday. You remember that experiment you did with the iron ring with a coil of wire on each side of it? When you sent an electric current through one of the coils, you got a new current generated in the other coil round on the other side of the ring."

Faraday: "Magneto-electric induction. Yes?"

Engineer: "Well, since then we've been able to do without the iron ring and also to move the coils farther and farther apart and still pick up the current in the second coil."

Faraday: "I could only separate them a few inches. How far can you do it now?"

Engineer: "As far as you like—half way round the world. We've got much more sensitive instruments and of course we use high frequencies. . ."

Faraday: "This is really wonderful. I. . ."

Engineer: "You don't know the half of it, sir. We can send music and people's voices and all sorts of messages all over the world with it!"

Faraday: "Might I see this thing?"

Engineer: "Sure." (The radio plays the closing passages of Schubert's "Ave Maria.")

Faraday: "But this is wonderful. This is beautiful."

Engineer: "Yeah. But just go on listening." (The music ends and is followed by the following commercial announcement.)

Announcer: "People with tape-worm are always hungry. At the first sign of hunger, take Kilslime Tape-Worm Tablets and play safe."

Faraday: (Profoundly shocked) "How very—ungenteel. Do you suppose anyone else heard that man?"

Engineer: "Half the population of North America has to listen to that sort of stuff 20 times a day."

Faraday: "But that is monstrous, shameful!"

Engineer: "Slime marches on."

Faraday: "In 1831 I earned a thousand pounds as a consultant, apart from my small salary at the Royal Institution. So that I might devote myself to my researches, I withdrew from all commercial work. Was it for this?"

Engineer: "It's not as bad as that really."

Faraday: "Could it be worse?"

Engineer: "The way I look at it is this. Pretty soon people are going to get wise to that sort of muck, and it'll be off the air. The big trouble hasn't been with using things wrong—it's been not using them enough: all those homes without electrical gadgets and all those farms without light and power."

Faraday: "You mean, then, that my discoveries may yet receive their full application?"

Engineer: "The way people have been talking, there's only one thing that will stop it, and that's another war."

Faraday: "Surely, surely, that can be prevented?"

Engineer: "I hope so. There's the United Nations and. . ."

Faraday: "But do *you* think it can be?"

Engineer: "Look, Mr. Faraday, I'm just a radio mechanic who likes to read and think. . ."

Faraday: "At your age, I was a book-binder's apprentice who liked to read and think."

Engineer: "Well then, I'll tell you. I'm in the radio game and maybe I think my fleas are antelopes, but I don't think those fellows at San Francisco made the most of their chances. Here, I'll show you something. Listen to this." [There follows a rapid sequence of station calls, like this: "This is the Voice of America—one of the United Nations." "Prague calling. . ." "+?=″QxZ-k$($)+=" (Engineer's voice, "That's Chungking, they aren't on in English till six.") "This is London calling—here is the news." "You are listening to Radio Center, Moscow."]

Faraday: "I am content. My time was not wasted."

Engineer: "You're darn right it wasn't wasted, Mr. Faraday. I think those men at San Francisco spent a lot of time worrying about some things that don't matter. What they should have done was to work out a scheme so that when two nations have a dispute, each side can state its case over the other country's radio network. That way, people couldn't be stampeded into things the way Hitler did. But I guess I'm just chasing rainbows."

Faraday: "I saw a rainbow once, at the bottom of a waterfall in Switzerland. There it remained motionless while gusts of cloud and spray swept furiously across its place and were dashed against the rock. It looked like a spirit strong in faith and steadfast in the midst of the storm of passions sweeping across it. And though it might fade and revive, still it held on to the rock, as in hope, and giving hope."

The Corrosion Resistance of Aluminum and Its Alloys

RONALD B. SPACHT

The National Bronze and Aluminum Foundry, Cleveland, Ohio

THERE is considerable confusion about the resistance of aluminum and its alloys to corrosion. The teacher impresses upon his students the fact that aluminum, which is very high in the electrochemical series, maintains its luster and resists corrosion much better than many metals beneath it. He may leave the impression that aluminum never corrodes and may be safely used at all places.

The housewife, too, is impressed with the noncorrosive properties of aluminum, since no special care is needed to maintain its luster. She may wonder why boiling tomato juice or vinegar increases the luster temporarily, but unless she has tried to make soap in an aluminum pan, she accepts the fact that aluminum is corrosion resistant. Even the alkali cleaners she may use are usually sufficiently inhibited so that they make no serious attack on aluminum.

On the other hand the industrialist may object to using aluminum because of fear of corrosion. If his fears are investigated, he probably has had corrosion difficulties in his plant or in his product when aluminum was substituted for some other metal. The author has seen aluminum castings severely corroded and pitted after a year or two of exposure to nothing more corrosive than well water containing several hundred parts per million of chloride ion.

When one considers the variety of conditions encountered by a modern industrial material, such as high temperatures, polluted atmospheres, polluted waters, salt water, and chemicals, it is not surprising that cases arise wherein a particular material such as aluminum fails in service.

Aluminum is attacked directly by many chemicals. Oxygen, as we all know, attacks readily but soon stops because of the formation of a protective oxide film. Aluminum owes its supposed inertness to this film; however, if anything destroys or removes this film, then the attack goes rapidly until the aluminum is consumed.

Alkalies, particularly sodium and potassium hydroxide, attack aluminum vigorously. Sodium hydroxide is one of the solvents used in the quantitative analysis of aluminum alloys. The attack is somewhat slower with trisodium phosphate and sodium carbonate. Disodium phosphate, sodium acetate, and sodium bicarbonate are practically without attack after long periods of exposure. Ammonia attacks aluminum very little, but suspensions of calcium hydroxide evolve hydrogen almost immediately. Since many agricultural spray solutions contain lime, aluminum should not be used for sprayers unless particular attention is paid to the selection of the alloy used in these sprayers.

Aluminum also reacts with acids. The extent of reaction depends upon the acid and upon the concentration and temperature of the acid. As expected, aluminum reacts only slowly with acetic acid and most organic acids, provided they do not contain chlorine. Aluminum tank cars are used to ship acetic acid, and many plants use aluminum piping and valves in its manufacture although some corrosion does take place.

If you have ever tried making aluminum nitrate from aluminum and concentrated nitric acid, you know that it cannot be done. Aluminum is resistant to nitric acid attack, particularly if the acid is concentrated. Concentrated nitric acid may be shipped in aluminum containers. Nitric acid is often used to clean aluminum objects of corrosion products and to neutralize aluminum objects after an alkaline dip.

Sulfuric acid reacts only slowly on aluminum at low concentrations, rapidly at 60 to 95 per cent concentrations, and very slowly above 95 per cent.

Hydrochloric and other halogen acids attack aluminum vigorously at all concentrations. In the quantitative analysis of aluminum alloys, mixed acids are often used. These mixtures usually contain sulfuric and nitric or sulfuric, nitric, and hydrochloric acids with some water added.

The action of inorganic salt solutions depends on several factors—namely, the ions composing the salt, the degree of hydrolysis, and to some extent the temperature and concentration. Aluminum tends to replace the heavy metals in the heavy metal salts. Thus, silver in silver nitrate is replaced rapidly and lead in lead arsenate is replaced if calcium hydroxide is present. Copper in copper sulfate is replaced slowly. Displacement reactions are slowed somewhat by the presence of oxide films, suggesting that the heavy metal salt must first break down this film before the reaction can proceed. Freshly polished strips of aluminum displace silver almost immediately from silver nitrate solutions, while anodized aluminum strips show very little reaction for 24 hours and then react rapidly.

In regard to the anion constituent, the chloride ion is the worst offender. Solutions of sodium and calcium chloride are corrosive to aluminum over long periods of time. In fact, chlorides are the worst natural corrosive agents of aluminum and its alloys. Most accelerated corrosion tests are carried out with sodium chloride solutions, sometimes with hydrogen peroxide added. The corrosive action of chlorides is probably due to the loosening of the oxide film which continually exposes fresh aluminum surfaces. Chromate ions usually inhibit the corrosion of aluminum.

Hydrolysis accounts for the action of sodium carbonate and sodium phosphate solutions upon aluminum.

On the acid side the effect is not so noticeable, since most dilute solutions of acids attack aluminum only very slowly. Ferric chloride solutions, however, react rapidly on aluminum test samples with the liberation of hydrogen and finally precipitation of ferric hydroxide.

Most organic liquids when pure do not attack aluminum; however, the presence of moisture and heavy metal impurities may lead to attack. Organic compounds containing chlorine may be corrosive. Alcohols attack when entirely free from water.

Gases such as carbon dioxide and hydrogen sulfide have very little effect upon aluminum. Moist sulfur dioxide and moist chlorine will attack.

A summary of the corrosion-resistant properties of aluminum can be found in a table prepared by Dix and Mears.[1] Selected data from a survey conducted by *Chemical and Metallurgical Engineering*[2] will be found in Table 1. This gives a fairly good summary of the material discussed so far.

The second method of corrosive attack upon aluminum is called electrolytic or galvanic corrosion. There is no hard and fast dividing line between those two methods of attack and hence the division made here is purely arbitrary. This type of corrosion is usually much more prevalent in exposed aluminum than the purely chemical attacks described above. Burns[3] and Brown[4] are the authors of two outstanding papers on this type of corrosion.

Burns says that electrolytic reactions are of the replacement type with the corroding metal replacing hydrogen from water. The metal ions go into solution at the anode while hydrogen ions are discharged at the cathode. In such corrosion processes the anode becomes the corroded member and the cathode is the protected member unless side reactions take place. For electrolytic corrosion to proceed, an electrolyte must be present. Furthermore, which element becomes the anode or cathode cannot always be predicted from the electrochemical series, since corrosive environments are usually much different from those under which electrode potentials are measured.

To illustrate from values given by Brown: aluminum has an electrode potential of -2.01 volts and zinc -1.10 volts, thus making zinc cathodic toward aluminum. But if the potentials of zinc and aluminum are measured in 1 M sodium chloride solution, then the aluminum potential is -0.86 and the zinc -1.15; in other words, aluminum is now cathodic toward zinc. In another example the electrode potential of iron is -0.78 and -0.37 for ferrous and ferric ions, respectively. In 1 M nitric acid aluminum drops from -2.01 to -0.49 and iron becomes -0.58; hence again the potentials are reversed from those in the electrochemical series.

TABLE 1

CHEMICAL CORROSION OF ALUMINUM

Substance	*Concentration (per cent)*		*Inches penetration per year (room temperature unless specified)*
Ammonia	10		0.057
Aniline	Pure		Pitted after 16 hrs. boiling
Sodium carbonate	10		0.33 (at 86°F.)
Sodium hydroxide	1		4.6
Sodium hypochlorite	5 (free Cl_2)		0.081 at 70°F.
Acetic acid	0.5		0.0013
	100		< 0.001
Carbonic acid	carbonated tap water		< 0.001
Citric acid	10		< 0.001 (at 86°F.)
Hydrochloric acid	0.25		0.005
	5		0.075
Hydrofluoric acid	0.1		0.7
	10		8.3
Mixed acids	H_2SO_4	HNO_3	
	90	4	0.90
	80	20	0.45
	80	5	1.24
	60	40	0.47
	40	60	0.38
	20	80	0.09
	20	55	0.14
Nitric acid	5		0.041
	20		0.11
	93		0.004 (at 135°F.)
	95		< 0.004 (at 135°F.)
Oleic acid	Pure		< 0.001
Phosphoric acid	10		0.074
	50		0.20
	85		0.24
Sulfuric acid	0.5		0.012
	25		0.060
	60		0.19
	95		0.37
	100		0.002
Sulfurous acid	3		0.0096
Tannic acid	10		< 0.001
Ammonium sulfate	5		None
Calcium chloride	Severe with heavy metal salts present		
Copper sulfate	10		0.011
Ferric chloride	1		0.11
Ferrous sulfate	1		0.001
Sodium nitrate	1		< 0.001
Sodium sulfate	1		< 0.001
Benzene	Pure		No attack
Butyl acetate	Pure		Stained only
Carbon tetrachloride	Severe at B. P. if unstabilized		
Ethyl acetate	Pure		None
Ethyl alcohol	95		Stained only
Ethylene glycol			Stained only
Formaldehyde	38		0.010
Glycerin	30		0.001
Methanol			No attack

The existence of electrolytic cells which cause corrosion results from a heterogeneity of the interface between the metal and its environment, arising from differences in composition or physical conditions of the metal surface or of the concentration of the environmental components. The following are some conditions which might lead to electrolytic corrosion: (1) a base metal and a noble metal; (2) contact of two different aluminum alloys with different electrode potentials; (3) inclusion of foreign particles such as dirt or iron in the surface of the aluminum object; (4) metal and metal oxide; (5) strained and annealed metal; (6) small grain size and large grain size; (7) metal in presence of oxygen and metal in the absence of oxygen.

Let us discuss these briefly. Corrosion may take place due to segregation within the alloy. When the solubility of a particular metal in aluminum is exceeded, pure crystals of this metal may separate upon cooling, resulting in local areas which lead to electrolytic corrosion in the presence of an electrolyte. Aluminum-copper alloys, particularly when the copper ex-

[1] DIX, E. H., AND R. B. MEARS, in S. L. Hoyt, "Metals and Alloys Data Book," Reinhold Publishing Corporation, New York, 1943, table 258.

[2] *Chem. & Met. Eng.*, **51**, 107–31 (1944).

[3] BURNS, R. M., *Am. Soc. Testing Materials Bull.* **126**, 17–20 (1944).

[4] BROWN, R. H., *ibid.*, pp. 21–6.

TABLE 2

WEIGHT LOSSES OF ALUMINUM DISCS IN PER CENT OF ORIGINAL WEIGHT

Metal	Coupled with	La Jolla, Calif.	Sandy Hook, N. J.	Key West, Fla.	Pittsburgh, Pa.	Altoona, Pa.	Rochester, N. Y.	New York State City	New York State College	Phoenix, Ariz.
Al	Al	2.3	0.05	0.03	0.02	0.04	0.01	0.04	N	0.1
Al	Cu	16.6	7.8	3.6	1.0	3.3	4.0	4.8	0.5	0.8
Al	Fe	8.3	1.3	2.7	1.5	2.0	1.7	4.4	1.4	1.4
Al	Pb	15.3	2.9	3.1	1.9	1.9	0.4	2.2	0.4	0.4
Al	Ni	6.0	0.8	1.5	0.6	1.3	0.2	1.3	0.3	0.1
Al	Sn	9.4	2.4	1.6	1.2	1.4	1.0	1.8	0.1	0.1
Al	Zn	0.6	0.2	N	N	0.1	0.1	N	N	N

ceeds one per cent, become subject to such corrosion, with the eight per cent copper alloys having very low corrosion resistances particularly in salt water.

The contact of aluminum with a more noble metal will lead to the corrosion of aluminum, and in general the more noble the metal the more rapid the corrosion. The A.S.T.M.[5] has published some data on metal couples exposed to various atmospheres. The results for aluminum couples are tabulated in Table 2.

La Jolla, Sandy Hook, and Key West represent typical salt-water atmospheres. Only the test discs at La Jolla were subject to direct spray from ocean water. Pittsburgh, Altoona, Rochester, and New York stations represent industrial atmospheres, with Altoona the worst and with New York City a combination of industrial and salt-water atmosphere. The State College station is a typical rural atmosphere with considerable humidity, while the rural station at Phoenix is a dry atmosphere.

Examination of the table shows several important things in regard to the electrolytic corrosion of aluminum. First, corrosion increases as the metal coupled with aluminum becomes more noble. Second, the greater the concentration of the electrolyte, the more rapid the corrosion. In fact, moisture alone is not harmful. Third, zinc which is anodic to aluminum, offers excellent protection to aluminum.

Contact of two different aluminum alloys may lead to electrolytic corrosion in the presence of an electrolyte. Thus, commercially pure aluminum is anodic to 17ST alloy by about 0.16 v. When one considers the numerous alloys and metals in a modern automobile or airplane, he wonders that corrosion is not worse than it is.

Inclusion of foreign particles such as dirt or iron on aluminum surfaces causes centers of different potential and hence leads to electrolytic corrosion. One case is reported of the spotted corrosion of aluminum sheeting,[6] caused by contamination from a drop hammer die composed of an alloy of bismuth, lead, and tin. When methods were worked out to prevent inclusion of die particles, the corrosion completely disappeared.

Dix and Mears[7] mention that the method of heat treatment of such alloys as 17S and 24S definitely affect the corrosion resistance of these alloys. They also mention that absorbent felt may cause corrosion due to the pick-up of moisture and by oxygen screening action.

Brief mention should be made of a particular type of corrosion known as stress corrosion,[8] which is the cracking produced under stress in certain atmospheres. Thus, stressed brass will crack when in contact with atmospheres of ammonia, even though little surface corrosion is evident. Aluminum alloys are subject to stress corrosion. It is thought to be electrochemical in nature. Stress failure is sometimes due to increased surface corrosion under load.

Another type of corrosion, sometimes found in automobile cylinder heads,[9] appears to be a combination of corrosion and erosion. Corrosion, in this case, is caused by the high chloride content of the coolant. Damage is caused at the places where the water hits the aluminum head at high velocities, suggesting that the chloride content of the water causes corrosion, then the water washes or tears away the corrosion products exposing a fresh aluminum surface for further attack.

From tables taken from A.S.T.M. tests [5,10] it can be seen that aluminum alloys compare very favorably with other alloys under most conditions. The amount of corrosion is dependent upon the type of atmosphere. Dry and unpolluted atmospheres are particularly noncorrosive to aluminum. Heavily polluted industrial atmospheres in moist climates lead to considerable corrosion, but even here, aluminum excels most of the alloys studied. Sea coast atmospheres are not particularly harmful unless direct contact is made with salt spray. In this one environment aluminum ranked below average in the A.S.T.M. tests.

Thus far the various factors causing corrosion of aluminum have been discussed. Obviously the means of preventing corrosion will depend upon the environment in which aluminum is placed. In some cases the chemical activity of aluminum precludes its use entirely, as for the handling of strong caustic solutions and chlorine compounds where inhibitive agents are not permissible. In other cases aluminum may be used if proper precautions are taken to prevent its corrosion. In still other cases little or no protection against corrosion is needed, as in cooking vessels.

Many times it is possible to eliminate corrosion difficulties by proper choice of alloy, provided other physical properties can be met. Commercially pure aluminum (99 per cent or more) is very resistant to corrosion and in most uses needs no protection. As alloying elements are added, corrosion resistance usually de-

[5] GORMAN, L. J., *Proc. Am. Soc. Testing Materials*, **39** (1939).
[6] HAYTHORNE, P. A., *Iron Age*, **156**, 72–3 (1945).
[7] DIX, E. H., AND R. B. MEARS, *S. A. E. Trans.*, **35**, 215–20 (1940).
[8] *Metal Progress*, **47**, 75–8 (1945).
[9] JARDINE, F., *S. A. E. Trans.*, **35**, 524–5 (1940).
[10] FINKELDEY, W. H., *Proc. Am. Soc. Testing Materials*, **44**, 224–39 (1944).

creases due to the unlike materials present on the surface of the metal which tend to become centers of electrolytic corrosion.

Dix and Bowman[11] state that the addition of copper in excess of the limit of solid solubility tends to lower the high resistance of pure aluminum to corrosion. No protection is necessary if thick sections are used, but if thin sections are used, then protective coatings must be employed. Solution heat treatment definitely improves corrosion resistance of these alloys over the annealed forms. In general, the corrosion resistance goes down as the copper content goes up; thus the 8 per cent copper alloys have less corrosion resistance than the 4 per cent.

Magnesium alloys readily with aluminum up to 10 per cent. Kempf and Keller[12] state that the resistance of cast aluminum-magnesium alloys to atmospheric and salt spray corrosion is excellent and is much less than the casting alloys of aluminum-silicon, aluminum-copper, or aluminum-zinc. The wrought aluminum-magnesium alloys are also the most resistant to alkaline corrosion of any of the aluminum alloys. Such resistance increases with magnesium content.

Silicon forms many alloys with aluminum, said to exhibit greater corrosion resistance than aluminum-copper alloys. These alloys are also said to be superior to aluminum-zinc-copper alloys. Since silicon has an electrode potential close to that of aluminum, this increased corrosion resistance is readily explained.

Another group of alloys is the aluminum-zinc group. Until recently these were not highly developed in this country, but with the announcement of 75S, R-301, and 40E containing 5 per cent or more of zinc this group tends to gain prominence. In Europe, with a shortage of copper, the aluminum-zinc alloys have tended to be used in place of the aluminum-copper alloys. Considerable disagreement exists in the literature as to the effects of zinc on corrosion resistance, but it is generally agreed that the presence of zinc and copper together is the real cause of poor corrosion resistance. As yet there seems to be some differences of opinion as to just how much copper can be present without greatly affecting the corrosion resistance of aluminum-zinc-magnesium alloys.

Of the minor constituents of aluminum alloys consideration should be given to iron, manganese, titanium, and chromium.

Iron is always present in aluminum, usually from 0.2 per cent to 1.50 per cent or more in some alloys. These amounts must be greatly exceeded before the iron is definitely harmful.

Manganese according to some authorities overcomes the harmful effects of iron and improves the corrosion resistance of aluminum alloys in general. There is evidence that the corrosion resistance of aluminum-manganese alloy approximates that of commercially pure aluminum.

Chromium is said to improve corrosion resistance. Titanium has little direct effect but due to its grain-refining properties might improve corrosion resistance from that angle. Tin above 0.2 per cent is said to be harmful.

Recent studies have indicated that a few of the rarer elements added in small quantities to aluminum alloys may improve their corrosion-resisting properties. Germanium is known to reduce corrosion resistance and fatigue. Cerium, used by Germany during the war, greatly improves aluminum castings, although as yet no claims are made for increased corrosion resistance. Undoubtedly other minor elements will be found which will give improved resistance to corrosion.

In general, any metal added to aluminum in excess of its solubility may increase its rate of corrosion, particularly if cathodic to aluminum. In this respect high aluminum-copper and high aluminum-copper-zinc alloys are the worst. High magnesium alloys are the most resistant to corrosion, particularly to alkaline solutions. High silicon alloys are better than high copper alloys. High zinc alloys are not bad if the copper content is kept low. Since an aluminum alloy is chosen for a particular part for reasons other than corrosion-resisting properties, alloys are many times used which are known to have low corrosion resistance. The problem then becomes one of preventing corrosion.

Careful attention by the engineer to the design and maintenance of aluminum objects can do much to eliminate corrosion. Designs should avoid contact between dissimilar metals and even different alloys of the same metal. Adequate drainage and ventilation should also be considered in design, since if aluminum can be kept dry, most of the corrosion difficulties are eliminated.

If dissimilar metals are used, they should be insulated. Periodic cleaning destroys the electrolytic cells set up by dirt or reduced heavy metals. Steel wool and wax are good cleaners, but uninhibited alkaline cleaners are harmful.

Chemical attack can often be stopped by use of appropriate inhibitors. Thus, sodium silicate inhibits the action of alkalies including sodium carbonate and sodium phosphate. Corrosive agents present in water, such as carbon dioxide, sulfur dioxide, and heavy metal salts, may be inhibited by use of sodium chromate and similar salts. Soluble oil inhibitors in concentrations of one per cent are the most effective inhibitors for chloride-containing waters used as coolants in automobile radiators.

Brown[13] and also Fink[14] suggest that aluminum may be protected by use of applied electrical currents. In the electrolytic corrosion of metals the corroding member is the anode; hence if aluminum can be made the cathode either by the application of external current or by connecting to a metal anodic to aluminum, its corrosion should be stopped. The author has tried this out on iron and aluminum strips immersed in salt

[11] DIX, E. H., AND J. J. BOWMAN, "Metals Handbook," A. S. T. M., 1939, p. 1249.
[12] KEMPF, L. W., AND F. KELLER, *ibid.*, p. 1257.
[13] *Loc. cit.*
[14] FINK, W. L., *ibid.*, pp. 1323–5.

solution and has been able to adjust the voltage so that little corrosion of either metal took place.

Brown also mentions that in the case of amphoteric elements such as aluminum, zinc, and lead, if the current density is too high, then the accumulation of hydroxide around the cathode is great enough to attack it severely. Such is the case with aluminum when the applied current is too high.

Designing so that the area of the cathodic alloy is small and the area of the anodic metal is large will also aid in corrosion control—at least, will spread corrosion of the anodic metal over a larger area.

Brown discusses briefly the use of a more anodic metal to control corrosion. Such control at the expense of a particular metal is called cathodic protection. Recently, buried magnesium bars[15] have been used to protect pipe lines from corrosion. If both electrodes of a couple can be made the cathode by a current from some other source, the galvanic corrosion of the couple can in many cases be prevented. The source of the current may be from an inert electrode with externally applied potential or from a metal more anodic than both of the two comprising the couple. The author has succeeded in practically eliminating the corrosion between an iron and aluminum couple by applying the proper external voltage.

The most widely used method of protecting aluminum is by use of protective coatings. Three classes of coatings may be applied—namely, metallic coatings, oxide coatings, and paint coatings.

Certain metallic coatings protect the aluminum core because they are anodic to the core and also have an initial high resistance to corrosion. Thus, "cladded" aluminum sheeting is made by coating high aluminum-copper alloys with commercially pure aluminum or other alloy which is anodic to it. Zinc is anodic to aluminum in most natural environments, hence offers excellent protection when applied as a coating.

Coatings which are cathodic to the aluminum base offer protection only until broken and then hasten its corrosion. Nickel and chromium coatings come under this category.

Oxide coatings are of two types, one produced by chemical means, the other by electrolytic means. The chemical method involves dipping the aluminum object in a dilute solution of hot sodium carbonate, followed by a sealing treatment in hot potassium dichromate. The oxide film is rather porous but serves as an excellent base for painting. A fairly hard corrosion- and abrasion-resistant oxide coating is formed by making aluminum the anode in an electrolytic cell. The electrolyte is either chromic, sulfuric, or oxalic acid. Best results are obtained with sulfuric acid. The film is attacked by certain salt solutions and alkalies, but for many uses needs no further treatment except sealing. It also serves as a paint base and can be dyed with certain organic dyes.

Fellom[16] reviews briefly the details of a good anodizing procedure. The castings are made the anode and suspended in a lead-lined tank which serves as the cathode. Aluminum racks are used to support the castings. To secure good anodizing, the castings must be clean. Some use inhibited alkaline cleaners, usually followed by a nitric acid dip. All iron inclusions and surface impurities should be absent. High silicon alloys are difficult to anodize unless they have been modified with sodium. In general, however, the presence of other alloying elements does not interfere with the sulfuric acid process.

The most widely used protective coatings consist of paints. To get best adhesion, the aluminum should be given an oxide coating either by chemical or electrolytic means. A phosphoric acid dip also prepares the aluminum surface for painting. A primer should be applied which does not contain lead or heavy metals. Zinc chromate is an excellent primer since it also acts as an inhibitor to corrosion. After the primer, almost any good lacquer can be used. The only requirement is that it have good adhesion and be impermeable to moisture.

Finally, careful foundry procedure is important if a given alloy is to have maximum corrosion resistance. Clean metal, clean metal pots, accurate temperature controls, avoidance of overheating, rapid handling of molten metal, elimination of segregation, and proper heat treatment all have a part to play in developing the maximum possibilities of a particular alloy.

[15] SMITH, A., JR., *Modern Metals*, **1**, 22–3 (1945).

[16] FELLOM, R., *Light Metal Age*, **2**, 23 (1944).

If a fragment of a sugar molecule darting through the solution in the blood stream or in the stomach juices crashes into a passing molecule, a part of the sugar may chip off and combine with the collision partner. The remaining fragment of the sugar molecule is left with its unsatisfied electrical charge, and this fragment may continue the process, chipping off and combining with a particle of another molecule. This repeated process is a chain reaction—just as the burning of a match and the explosion of dynamite are chain reactions.—Hugh S. Taylor

Report of the NEW ENGLAND ASSOCIATION of CHEMISTRY TEACHERS

EIGHTH SUMMER CONFERENCE

TWO symposia will feature the Eighth Annual Summer Conference of the New England Association of Chemistry Teachers at Middlebury College, Middlebury, Vermont, August 19–24. Professor Ernst Hauser of the Massachusetts Institute of Technology, Cambridge, Massachusetts, will lead a symposium on "Colloids," while Professor William B. Meldrum of Haverford College, Haverford, Pennsylvania, will lead a symposium on "Electrolytes."

The Conference will include a discussion of the incorporation of chemical advances made in World War II into the chemistry curriculum. A wide variety of interests will be covered, as, for example, the discussion on "Catalysts in the Petroleum Industry" by Dr. Ben B. Corson of Bethlehem, Pennsylvania; "Steel" by Dr. Joseph Libsch of Lehigh University, Lehigh, Pennsylvania; and a discussion of the "Electron Microscope."

Attendance at the Conference is not limited to members of the New England Association of Chemistry Teachers or to New England residents, and the event is becoming one of more than regional importance from year to year. Nonmembers of the Association may attend for a modest membership fee that includes a year's subscription to the JOURNAL OF CHEMICAL EDUCATION. The entire Conference is set up on a low-cost family basis, and it will include teas, a picnic, industrial trips, and outings, as well as chemical discussions. Further information may be obtained from Professor Ina M. Granara, Simmons College, Boston 15, Massachusetts, who heads the Conference Committee.

Middlebury College, host to the Conference, is located in the southern part of the Green Mountains, an ideal, cool vacation spot. The college body, normally about 600 students, studies a liberal arts program. Dr. P. Conant Voter is Chairman of the Chemistry Department at Middlebury.

WILBUR E. BRADT

The necrology committee regrets to report the death at his family home in Washington, D. C., of Lieutenant-Colonel Wilbur E. Bradt.

Lieutenant-Colonel Bradt served in the Pacific Theater from sometime in 1942 until the close of action. An associate in Washington reports that "his war experiences had been especially harrowing, since of his original command, only one survived beside himself." He leaves a widow and two children.

S. Walter Hoyt, *Chairman*
Necrology Committee

NEW MEMBERS

John R. Gow, Westminster School, Simsbury, Connecticut
James L. Shea (College of Our Lady of the Elms), 42 Naomi Street, Chicopee Falls, Massachusetts
Mary of the Cenacle, R.J.M. (Catholic Teachers' College), 164 Harrison Street, Providence 7, Rhode Island
Edward R. Linner, Vassar College, Poughkeepsie, New York

NOTES

Mr. E. C. Weaver of Phillips Academy, Andover, Massachusetts, has been appointed representative of the New England Association of Chemistry Teachers on the Board of Directors of the National Science Teachers' Association.

Mr. Standish Deake is now at Wentworth Institute, Boston, Massachusetts.

OFFICIAL BUSINESS

232nd Meeting, October 27, 1945, St. Paul's School, Concord, New Hampshire.

The following program was given at the 232nd meeting of the N.E.A.C.T.: "Postwar Trends in Science Teaching," John C. Hogg, The Phillips Exeter Academy; "Synthesis of the New Elements, Neptunium and Plutonium," Laurence S. Foster, Massachusetts Institute of Technology; "Demonstrations," David L. Davidson, Gustavus J. Esselen, Inc., and Elbert C. Weaver, Phillips Academy, Andover; "Leaf Pigments," Samuel E. Kamerling, Bowdoin College. A short business meeting preceded the afternoon lecture.

233rd Meeting, December 8, 1945, Simmons College, Boston, Massachusetts. (Held jointly with the New England Association of Biology Teachers and the Eastern Association of Physics Teachers.)

The following program was given at the 233rd meeting of the N.E.A.C.T.: "Polarized Light in Physics, Chemistry, and Biology," Edgar Barr, Polaroid Corporation, Cambridge; "New Goals in School Health Programs," Curtis M. Hilliard, Simmons College; "Textile Research Looks Ahead," Edward R. Schwarz, Massachusetts Institute of Technology; "Description and Demonstration of Surplus Property Electronic Equipment Available for Schools," L. B. Arguimbau, Massachusetts Institute of Technology; "Electronic Theory of Acids and Bases," William F. Luder, Northeastern University. A short business meeting preceded the afternoon lecture.

234th Meeting, February 2, 1946, Rhode Island College of Education, Providence, Rhode Island.

The following program was given at the 234th meet-

ing of the N.E.A.C.T.: "Phosphate Chemistry," R. L. Copson, Rumford Chemical Works; "Astronomer Looks at the Atomic Bomb," Charles H. Smiley, Brown University; "Motion Pictures and Demonstrations," John Gammons Read, College of Education. A short business meeting preceded the afternoon lecture.

235th Meeting, March 16, 1946, College of Our Lady of the Elms, Chicopee, Massachusetts.

The following program was given at the 235th meeting of the N.E.A.C.T.: "The Forces Between Atoms, Ions, and Molecules," John A. Timm, Simmons College; "Surface Phenomena in Carbon Blacks: The Bearing of Heats of Adsorption on the Problems of Rubber Reinforcement," Ralph A. Beebe, Amherst College; "Poison Ivy," G. Albert Hill, Wesleyan University; "The Structure of Gliotoxin," Milton D. Soffer, Smith College. A short business meeting preceeded the afternoon lectures.

Members of the association are requested to send the names of people who might be interested in joining the N.E.A.C.T. to the secretary, Miss Dorothy W. Gifford, Lincoln School, Providence 6, Rhode Island.

A Device for Teaching Chemical Arithmetic

HORACE G. DEMING

University of Nebraska, Lincoln, Nebraska

STUDENTS in elementary chemistry perhaps more frequently fail or drop out on account of inability to grasp chemical calculations than for any other single reason. The most successful remedy we have found, during years of experimenting with different methods, is the annexed diagram which relates all the important types of problems that are based on chemical equations, points out logical sequences of steps to be taken, and helps train the student to explain clearly how he arrives at his answers. The purpose last mentioned is deserving of much more emphasis than it usually gets.

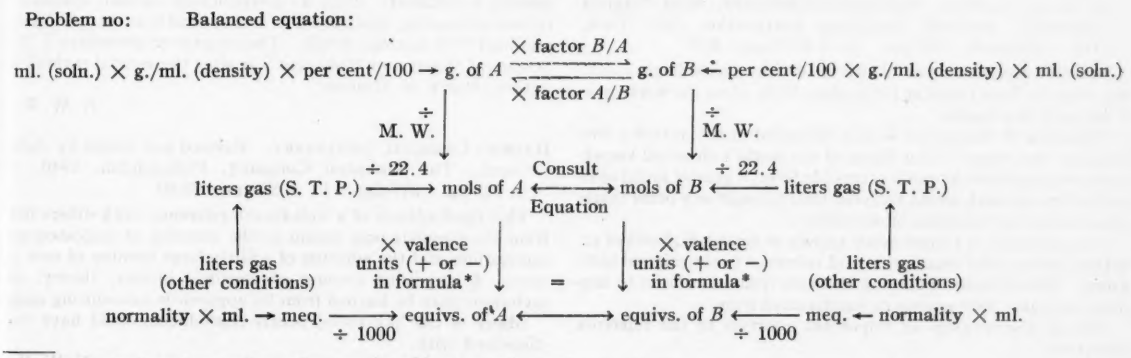
The operations summarized in different parts of the diagram are explained in a number of successive lectures. Then a sheet is mimeographed that repeats the diagram eight times, with a few textbook references included. This provides a standard form for working eight problems.

The student enters the data given for substance A, then shows what result he gets for each step until he arrives at the answer, which may relate to substance A or to another substance B that reacts with or is related to A in a known chemical reaction. When he has found the number of mols of one substance, he may "cross over" to the other by referring to the balanced chemical equation which shows how many mols of the one correspond to any known number of mols of the other.

When both substances are ionic or when they serve as oxidant and reductant, the number of equivalents or milliequivalents of the one is *equal* to the number of the other. Various short cuts soon become evident. For example, it is observed that the volumes of reacting gases are in the same ratio as the numbers of mols in the balanced chemical equation.

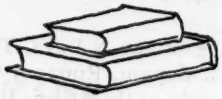
Chemical factors may be mentioned as a short cut from *grams* to *grams*, to be used chiefly by analytical chemists, who may need to solve hundreds of such problems, all based on the same chemical equation. A slight modification of the diagram will provide for problems based on engineering (English) units.

Students are directed to trace each problem through, setting down the result obtained in each step on the way to the final result, then to check the work by tracing it backward, each former operation being reversed. Practically everyone becomes nearly infallible by the time he has worked enough problems of assorted types to fill two or three record sheets. Then he abandons this crutch of his own accord.


Problem no:
Balanced equation:
ml. (soln.) × g./ml. (density) × per cent/100 → g. of A
× factor B/A
× factor A/B
g. of B ← per cent/100 × g./ml. (density) × ml. (soln.)
÷ M. W.
÷ M. W.
÷ 22.4
Consult Equation
÷ 22.4
liters gas (S. T. P.) → mols of A ↔ mols of B ← liters gas (S. T. P.)
liters gas (other conditions)
× valence units (+ or −) in formula*
=
× valence units (+ or −) in formula*
liters gas (other conditions)
normality × ml. → meq.
÷ 1000
equivs. of A ↔ equivs. of B
meq. ← normality × ml.
÷ 1000

* Use change in valence when substance is oxidant or reductant.

RECENT BOOKS



FLUOROCHEMISTRY. *Jack De Ment*, Associate Editor, *Mineralogist Magazine;* Head, Fluorescence Laboratories. Chemical Publishing Company, Inc., Brooklyn, 1945. xvii + 796 pp. 30 figs. 146 tables. 15.5 × 23.5 cm. $14.50.

An authoritative modern treatise on the theory and applications of luminescent systems would be a valuable addition to the literature. Unfortunately, "Fluorochemistry" falls far short of this goal.

"The fields of fluorescence, phosphorescence, luminescence, and radiation have been rather unfortunate by being encumbered with a too voluminous and somewhat ambiguous vocabulary," according to De Ment. To correct this situation, he undertakes to provide a nomenclature in which ". . . . every term should have a definite and clear meaning." Typical of the terminology considered precise and meaningful are "macro-activation" and "micro-activation," defined, respectively, as "incorporation of a large amount of a substance in another substance, without which the emission characteristics are not observed" and "incorporation of a micro or very small amount of a substance in another substance, without which the emission characteristics are not observed." "Macro-" and "micro-luminescence," along with many other terms, are similarly introduced or defined with the selfsame lack of rigor that the author so strongly deplores.

The theoretical aspects of luminescence are treated in large part by the methods of allusion and illusion, and their presentation is poorly integrated. A rather surprising feature of this section of the book is the application of the author's name to certain well-known principles which he claims to have been the first to discover or enunciate (circa 1942–43), for example, the "De Ment Absorption Law." This curious attitude with regard to the field covered by the book and his contribution to it is evident throughout the volume, being foreshadowed in the preface where De Ment offers to "introduce you to my science: *Fluorochemistry*, a newly established branch of human endeavor (which) has come into its own."

The book contains tabulations of the properties of large numbers of luminescent organic substances and minerals as well as an extensive but rather uncritical survey of synthetic inorganic phosphors, which in many places reduces to a patchwork of excerpts from the scientific and patent literature. The last part of the book is devoted to a discussion of "Fluorobiology," which deals with the theory and application of luminescence in biology.

The paper and printing are quite good. The illustrations are very few for a book of such size and scope, and many of the graphs are very crudely drawn. The greatest value of the book lies in the extensive bibliography.

J. H. SCHULMAN

SYLVANIA ELECTRIC PRODUCTS, INC.
SALEM, MASSACHUSETTS

ENCYCLOPEDIA OF CHEMICAL REACTIONS. Compiled and edited by *C. A. Jacobson*, Professor of Chemistry, West Virginia University. Reinhold Publishing Corporation, New York, 1946. Volume I. 804 pp. 15 × 23.5 cm. $10.

The first announcement of this book (then only in prospect) was made in THIS JOURNAL in October, 1933, when the work upon it had only just begun.

The scope of the project is best indicated in the author's own words at that time: "If a digest of the world's chemical knowledge were available in easily accessible form, a greater impetus to productive research would be given than through any other single achievement in the realm of chemistry."

It is proposed to record every known or reported chemical reaction, with a brief description and reference to the original literature. This volume, including elements from aluminum to bromine, contains 3073 entries in standardized form.

This is undoubtedly an important addition to the reference literature.

—N. W. R.

COLORIMETRY FOR CHEMISTS. *M. G. Mellon*, Professor of Analytical Chemistry, Purdue University. The G. Frederick Smith Chemical Company, Columbus, 1945. vii + 133 pp 51 figs. 10 tables. 15 × 23 cm. Paper cover, gratis. Bound, $1.00.

This booklet, as its title implies, was written from the viewpoint of the chemist. The term "colorimetry" includes both the measurement of color as color, and of color, *i. e.*, light-absorptive capacity, as related to the concentration of some desired constituent. With the advent of photocells, instruments for the measurement of color have appeared in great variety, and many analytical methods involving color measurement have been developed. Hundreds of papers and many books on colorimetry have been published during the past twenty years.

"Colorimetry for Chemists" is an outline of colorimetry, presenting a perspective of the problems involved and of the means of meeting them. There are six chapters; the first is devoted to definitions, perspective, and the chemistry in colorimetry; succeeding chapters deal with color stimulators, color comparators, filter photometers, spectrophotometers, and experiments in spectrophotometry. The booklet concludes with a bibliography of 251 references and an adequate index. It will be helpful to analytical chemists in general, and will serve as a useful guide to those entering this interesting and rapidly expanding field of analytical chemistry. The booklet joins the list of about a dozen pamphlets on various topics in analytical chemistry published in recent years by The G. Frederick Chemical Company. Both author and publisher are to be congratulated and thanked.

JOHN H. YOE

UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA

TIME, NUMBER AND THE ATOM. *R. Fortescue Pickard.* Williams and Northgate, Ltd., London, 1945. vii + 92 pp. 22.5 × 15 cm. 8/6*d*.

Arithmetical legerdemain in which the magic numbers are 43 and, to a lesser extent, 23, 37, and 79. To the reviewer the numerical patterns which the author has discovered among the mass numbers of the elements are of such little significance that a detailed review seems unjustifiable.

JOHN A. TIMM

SIMMONS COLLEGE
BOSTON, MASSACHUSETTS

ENGINEERING PREVIEW. *L. E. Grinter, Harry N. Holmes, H. C. Spencer, Rufus Oldenburger, Charles Harris, R. G. Kloeffler and V. M. Faires.* The Macmillan Company, New York 1946. x + 581 pp. 415 figs. 15.5 × 24 cm. $4.50.

Here is material for the high-school senior or college freshman who wants to orient himself in the basic material on which engineering is founded. After an introductory section, chemistry, technical drawing, mathematics, and several branches of physics are dealt with in some detail. The chapter on chemistry ("The Science of Water and Molecules") is after the general style of its author, Harry N. Holmes.

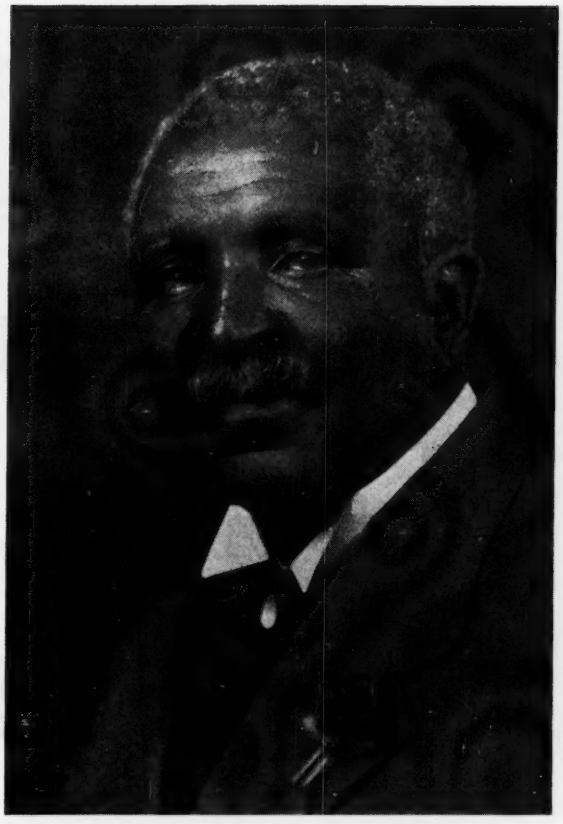
—N. W. R.

HACKH'S CHEMICAL DICTIONARY. Revised and edited by *Julius Grant.* The Blakiston Company, Philadelphia, 1946. xii + 925 pp. 217 figs. 17 × 25 cm. $8.50.

This third edition of a well-known reference work differs little from the previous ones except in the omission of indicated pronunciations and the addition of a fairly large number of new entries. A surprising amount of chemical history, theory, and technique may be learned from its apparently uninspiring pages.

Many of the half-tones, poorly reproduced, could have been dispensed with.

—N. W. R.



George Washington Carver (1864–1943)

See page 268

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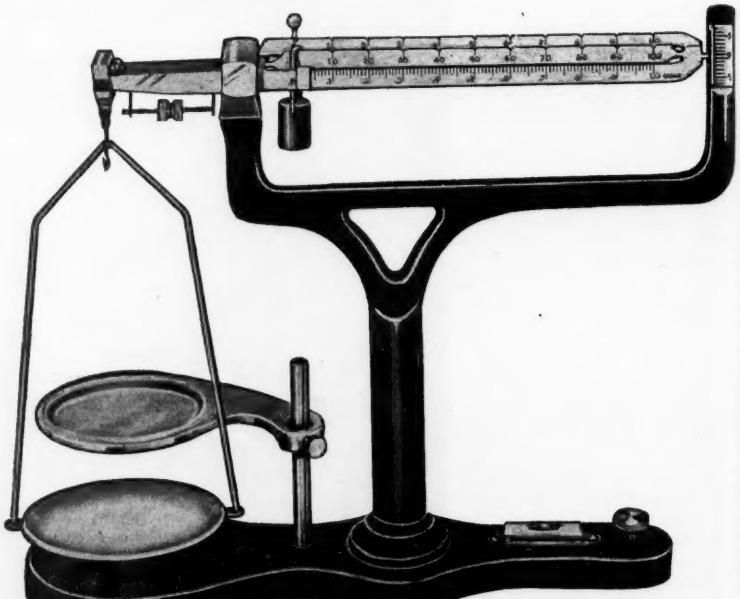

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Editor's Outlook

NO MORE now than at any other time can one safely believe all he hears, nor take at face value the significance of events. Nevertheless, if the closing remarks of the Secretary of War in his address at the Atlantic City meeting of the American Chemical Society are really indicative of the trend of military thinking, there will be something new in the world, after all. He said:

> Experience in World War I brought out the need for teamwork between industry and the fighting forces. That lesson was learned. World War II has added science as an indispensable member of the team. That lesson, too, has been learned. In all planning we must embrace the scientific research potential in establishing measures for national security, until the happy day comes, if it does come, when world peace may be an accomplished fact. Until that time organized science must accept the responsibility that its importance to the national security places on it.

To the end of strengthening the "team" it is proposed to (1) commission more scientifically trained men in the Army, (2) train more commissioned officers in science, and (3) offer better inducements to civilian scientists to work with the Army.

Well, that's one way to make a *start*, at least. The trouble is that the Army has never been an environment in which science could thrive healthily, and that situation is not likely to be improved by anything short of a revolutionary change in the military habit of thought. The secrecy, the gold-bricking, the buck-passing, the lack of imagination, the refusal to take responsibility because the next higher-up may step on you—these are some of the stone walls against which the scientist wears himself out in his dealings with the military. There is nothing humble about the Army in its relations with others. If the idea is to take science into camp and put it to work, the results will be about the same as from any other assignment to "K.P." duty. But if science is to have an *independent* and co-equal position in a council based upon unification of the Forces, that is quite another matter and something to look forward to.

Is this a belated recognition of the fact that scientists and the "production army" are as important in winning a war as the "combat army?" That is the face value of the statement, at least. Does it mean that if we ever have to do it again we will have a different theory behind Selective Service? The new theory doesn't seem to be altering the remnants of our present System. In other words, is the Army *really* going to change its attitude toward science and scientists?

What are the chances? Judge by the Army's attitude toward the current problem of control of "atomic energy." Hush-hush, secrecy, keep everything under wraps until everybody else knows about it, don't let anyone know what anyone else is doing for fear you might help him to make a discovery. Scientists put up with that sort of thing in wartime because they have to, but they won't work under such conditions normally. If the Army insists upon keeping science in chains it will not get much cooperation.

For the most part, we believe in the democratic ideal. We confirm everyone in the right of free speech; everyone has the privilege of speaking the truth as he sees it. Our political structure is based upon the theory that the truth will always be beneficial, no matter how much it hurts. Anyone may freely, if conscientiously, criticize the government and anyone in it. Let the truth prevail!

That far, at least, our politics follows the abstract path of science. But apparently we don't believe in pushing the policy too far. "There are certain things which, for their own good, our people ought not to know. There are certainly things which, for *our* good, *other* people ought not to know." That sort of thing may be expediency; it certainly is not consistent with the scientist's kind of thinking; it is not consistent with our normal kind of democratic political thinking. In fact, it borders close on some types of thinking that we were recently contending against to the death.

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HAROLD H. STRAIN

Carnegie Institution of Washington, Division of Plant Biology. Stanford University, California

UNIQUE reactive yellow pigments, usually found associated with fats, are essential constituents of the organic world. Without continual replenishment of these necessary materials by natural synthesis, few living organisms could long survive.

Somewhere in a past geological age rudimentary cells produced the first of these strange yellow substances. Later, more of the remarkable colored compounds appeared, and in time elementary plants used them in new life processes. Eventually, animals feeding upon plants employed the ever-present yellow constituents for regulation and control of vital reactions in their own bodies.

After eons of time man became curious about the widespread nutritional diseases that he observed in his domesticated animals and in members of his own clan. Some of these diseases were curable with special foods. Nearly 4000 years ago " . . . the liver of an ass, raw . . . " was prescribed for failure of vision in dim light. In the 19th century cod-liver oil became a popular supplemental food. But not until the 20th century were certain yellow plant pigments recognized as the primary source of a curative substance in liver.

Distinguished by their preferential solubility in fats and in fat solvents, these yellow plant products have now been found in a variety of organisms. The pigments themselves occur in numerous modifications which exhibit different physiological activities.

Recognition of the individual pigments and their complex physiological roles was dependent upon development of new physical, chemical, and biological techniques. It required careful correlation of diverse and apparently unrelated observations.

Earliest chemical investigations of yellow fat-soluble pigments were confined to the carotene of carrots. By 1837, however, the Swedish chemist, Berzelius, had found a similar yellow substance in autumn leaves. It was different from the familiar carotene, and he realized that it must be a new chemical compound. For his find, he coined the term "xanthophyll" from the Greek words meaning "leaf-yellow."

Discovery of xanthophyll marked the beginning of a fine distinction between two similar types of fat-soluble yellow pigments. Carotene was readily soluble in petroleum ether and was *not* extractable therefrom with aqueous alcohol. Xanthophyll, by contrast, was less soluble in petroleum ether and *was* extractable from it with aqueous alcohol. In time, chemists correlated these differences in solubility with the chemical composition of the pigments.

In the past 50 years some 70 or 80 xanthophylls and approximately a dozen carotenes have been isolated from plants and animals. Known collectively as carotenoids, they are the commonest yellow, orange, and red pigments in the organic world. The detection of these similar compounds in various organisms, their isolation, and the determination of their properties and chemical structures provide one of the most interesting stories in the field of modern research. This story embraces progress in practical and theoretical fields. It has been written by biologists, chemists, physicists, engineers, and farmers. It hinges upon such basic phenomena as the nature and function of vitamins and the maintenance of life by plants. It illustrates the complexity of relationship among agriculture, food processing, nutrition, and health.

SOURCES OF XANTHOPHYLLS AND CAROTENES

First hints of the wide distribution of xanthophylls and carotenes in nature came in 1860 and 1864 when these yellow pigments were detected in the green parts of plants. All green plants examined thus far, ranging from the smallest unicellular diatoms to the largest trees, contain both xanthophylls and carotenes. Here these pigments occur in intimate association with the

green chlorophylls—one part of carotene with about three parts of xanthophyll and 12 parts of chlorophyll. All these pigments, the green masking the yellow, are found within the plant cells in microscopic highly specialized bodies called "chloroplasts."

Formation of the yellow carotenoid pigments in leaves often precedes synthesis of the green chlorophylls. This is especially striking in leaves that have never been exposed to light. Young plants obtained by germination of seeds in the dark and young leaves of celery and of other blanched vegetables owe their pale yellow color to the presence of carotenoids. Upon exposure to light these immature plant parts form large quantities of chlorophyll and additional amounts of yellow pigments.

Xanthophylls are the principal coloring matter of specialized parts of many plants. Thus oranges, red peppers, fruit pods of the Chinese lantern, and the petals of many flowers, such as those of marigolds and the California poppy, owe their striking color chiefly to the presence of distinctive xanthophylls. Other plant parts such as carrots and tomatoes are colored by carotenes. During the early stages of their development, many of these plant parts are usually green. Later the special xanthophylls and carotenes are formed as the green pigments disappear, a phenomenon observed by most housewives in the ripening of oranges, tomatoes, and peppers.

Many fish, the feathers of some birds, shells of shrimps, crabs, and lobsters, and fats of many animals contain carotenoid pigments. In animals these pigments usually occur in solution in the fat or in combination with protein. Rupture of the union between protein and xanthophyll accounts for the change in color observed when crustacea are boiled.

For the most part carotenoid pigments found in animals are derived from plants which are consumed as food. But absorption of xanthophylls and carotenes from the food is a highly selective process. For example, the natural coloring matter of butterfat is carotene and that of eggyolk is xanthophyll. This selection occurs even when cows and hens receive rations equally rich in both pigments.

FUNCTIONS OF XANTHOPHYLLS AND CAROTENES

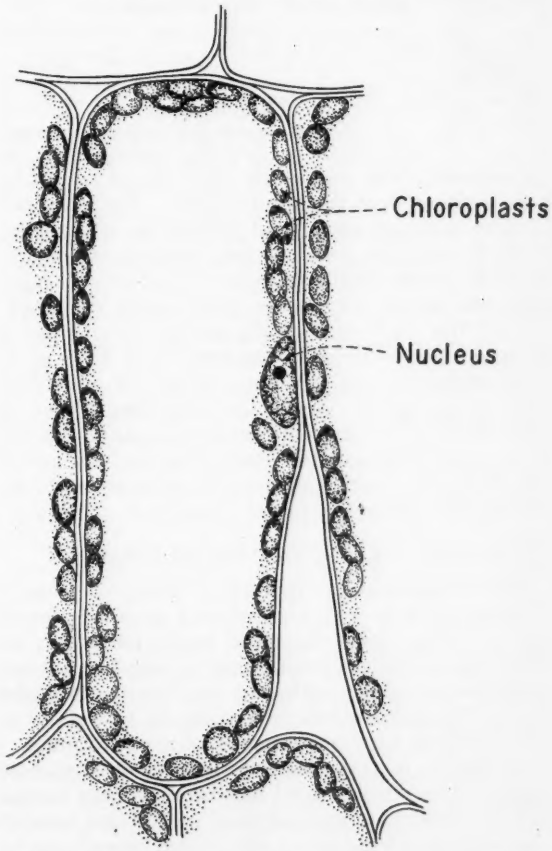
One of the most important roles that can be ascribed to some xanthophylls and carotenes is their conversion into colorless fat-soluble vitamin A in the animal body. From certain of these carotenoid pigments animals synthesize this vitamin which is essential for growth of the young and for formation of substances that render the eye sensitive to weak light.

In some fishes and in some birds the yellow markings that apparently serve as protective coloration are due to xanthophylls and carotenes. Other functions are indicated by the wide distribution of carotenoids in the animal kingdom and by the preferential concentration of these pigments in tissues exhibiting great metabolic activity.

Yellow fat-soluble pigments apparently play several important roles in plants. Coloration of flowers by carotenoids may serve to attract pollination insects. Curvature of plants toward light probably results from action of the light upon yellow pigments within the sensitive cells. This or a similar response may regulate the growth and development of many plants.

Xanthophylls and carotenes, in conjunction with chlorophylls, help maintain the universe of living organisms. Virtually all living beings, animals as well as plants, depend upon synthetic reactions that take place in the chloroplasts. Through absorption of sunlight chloroplast pigments garner the energy required for conversion of carbon dioxide and water into organic substances such as soluble sugars, starch, and cellulose. This photosynthetic process is basic to all agricultural production. It provides the primary foods of all animals as well as of man.

Is the presence of this triumvirate of xanthophylls, carotenes, and chlorophylls necessary for utilization of solar energy by plants? Recent experiments indicate that it is. Every plant that carries on photosynthesis contains these green and yellow substances. Light absorbed by pigments of each group is utilized in the



GREATLY MAGNIFIED CROSS SECTION OF PART OF A GREEN LEAF SHOWING A LEAF CELL AND ITS CHLOROPLASTS. THESE MICROSCOPIC CHLOROPLASTS CONTAIN THE YELLOW AND THE GREEN LEAF PIGMENTS.

photosynthetic process. Plants that lack the pigments are unable to utilize solar energy.

Ancient man in his pastoral world recognized all flesh as grass. Modern man with his analytical instruments sees all flesh as sunshine, condensed by the green and yellow chloroplast pigments.

COMPLEXITY OF THE NATURAL MIXTURES OF CAROTENOIDS

Mixtures of carotenoids occur in the green parts of all plants. In the past decade the existence of two leaf carotenes and of about a dozen leaf xanthophylls has been established. Leaves of all the higher plants that have been investigated contain most of these xanthophylls in approximately the same proportions. Some of the lower plants, such as bacteria and seaweeds, include mixtures of still other xanthophylls. Plants belonging to different botanical groups often do not have a single xanthophyll in common. Thus the unicellular diatoms and dinoflagellates, the two principal plants of the seas, contain mixtures of xanthophylls not found in land plants.

XANTHOPHYLLS OF HIGHER LAND PLANTS AND OF THE UNICELLULAR WATER PLANTS, DIATOMS, AND DINOFLAGELLATES

Diatoms	*Dinoflagellates*	*Higher plants*
Neofucoxanthin A	Neoperidinin	Neoxanthin
Neofucoxanthin B	Peridinin	Flavoxanthin
Fucoxanthin	Neodinoxanthin	Violasanthin
Diadinoxanthin	Neodiadinoxanthin	Zeaxanthin
Diatoxanthin	Dinoxanthin	Lutein
	Diadinoxanthin	Cryptoxanthin

Carotenes of the green parts of plants are subject to less variation than the xanthophylls. The principal carotene of marine and of land plants is the same, being identical with the principal *beta*-carotene of carrots. In some plants small quantities of additional carotenes are found. Of all the green plants examined, only in the photosynthetically active bacteria has a group of entirely different carotenes been discovered.

Xanthophylls and carotenes of specialized yellow fruits are subject to tremendous variation. Some of these pigments occur in only one or two sources. Some have never been found in fruits that are still green. In a few plants these pigments of fruits represent labile structural modifications of the commonest carotenoids.

ISOLATION OF XANTHOPHYLLS AND CAROTENES

Determination of the properties of organic compounds such as the carotenoids is contingent upon isolation of the substances themselves in a highly purified state. Since carotenoid pigments occur in small quantities (from three- to four-tenths of a gram in one thousand grams of fresh leaves) and since they are very reactive, this condition has been extremely difficult to fulfill.

Resolution of these natural mixtures of carotenoid pigments into their several members has been carried out by broadening an analytical trail blazed over 30 years ago by a Russian botanist named Tswett. In its present form his unique adsorption analysis leads to preparation of pigments in a high degree of purity. It is now widely utilized by chemists for isolation, separation, and identification of many types of different compounds.

The original basis of this novel and useful method was the observation that petroleum ether extracts of dried leaves form a series of green and yellow bands or zones when passed through glass tubes filled with very dry, powdered, adsorptive chalk. Separation of pigments into discrete bands on these chalk columns was enhanced by washing the adsorbed materials with fresh portions of the solvent.

Isolation of pigments separated by this "chromatographic adsorption" method is a simple matter. The colored bands are loosened one by one with a long spatula and transferred to separate vessels where they are agitated with alcohol. This solvent liberates the pigment from the adsorbent. Removal of the adsorbent by filtration provides solutions of the pure pigments. Concentration of the solutions by evaporation of the solvent yields glistening orange or red crystals of the carotenoid.

Successful application of the adsorption method depends upon careful selection of adsorbents and of solvents. With columns composed of a specially prepared magnesia or of lime, relatively large quantities of pure carotenes and xanthophylls have now been isolated from plants of many different species. For separation and isolation of carotenes petroleum ether is used for solution of the pigments. Separation of the xanthophylls is accomplished with a mixture of petroleum ether and acetone or with dichloroethane as solvents. Chlorophylls and certain labile algal xanthophylls are readily separable upon columns of powdered sugar. With this adsorbent, separation of the pigments is enhanced by use of petroleum ether containing about one per cent alcohol as solvent.

Chromatographic adsorption is the only procedure by which many natural mixtures of the chloroplast pigments have been resolved. These labile substances, so closely related chemically that they cannot be separated by the usual analytical methods, yield readily to the selective forces in the adsorption columns. The great resolving power of the adsorption technique, now widely appreciated in other fields, has made possible purification and estimation of the pigments and determination of their physical, chemical, and physiological properties.

PROPERTIES OF CAROTENOID PIGMENTS

Xanthophylls and carotenes are extremely sensitive and reactive substances. In organisms they are protected by the activities of the living cells. If the cells are killed, the pigments are destroyed by oxygen. This oxidative reaction is accelerated by enzymes and by light.

In solution carotenoids are partially converted into labile interconvertible isomers by light, by gentle heat, and by iodine and other similar catalysts. They are decomposed by acids, heat, and oxygen, changing gradually to colorless products. Like the reactive filaments of incandescent lights, carotenoids must be

preserved in evacuated and sealed glass tubes. In nature they persist for long periods only in the cold, dark, oxygen-free ooze of the ocean floor.

Results of both practical and theoretical significance have come from studies of the intense orange color of the xanthophylls and carotenes. Many careful investigations with the spectroscope have shown that each carotenoid absorbs slightly different proportions of blue and green light. This property, the absorption spectrum, is now widely used for identification of the individual pigments. It is intimately related to the arrangement of the atoms within the pigment molecules. It discloses some of the innermost secrets of chemical structure. Changes in the structure of the chromophoric portion of the molecule are accompanied by changes in the absorption spectrum. From determinations of the amount of light absorbed by the colored constituents in extracts of plants and animals the quantity of pigment contained in these sources can be found.

CHEMICAL STRUCTURE OF CAROTENOIDS

Physiological as well as physical and chemical properties of the carotenoids are reflections of the arrangement of the atoms in their molecules. For example, this molecular structure determines whether or not a carotene or xanthophyll will yield vitamin A in the animal body. Knowledge of the structure also reveals the chemical relationship between carotenoids and other organic compounds. It serves as the only reliable guide in attempts to synthesize the natural pigments.

In order to determine the structure of a newly discovered carotenoid, the organic chemist first ascertains the nature and the number of atoms in its molecule. His next and most difficult task is the determination of the spatial arrangement of these atoms. From a vast amount of experience he knows that molecules of organic substances are composed of a skeleton of carbon atoms linked together by bonds or units of chemical affinity. Each carbon atom has four of these bonds distributed equidistant about it. It is joined to neighboring carbon atoms by various combinations of single C—C, double C=C, or triple C≡C bonds to form chains, plane rings, or complex three-dimensional structures. Chemical bonds not utilized in combinations between carbon atoms always occur in union with atoms of other elements, chiefly hydrogen and oxygen. The variety of structures that may be built from carbon atoms is enormous, but for every organic substance there is only one structure for each of its molecules.

With his new carotenoid the chemist determines the number of double bonds and the number of rings of carbon atoms present in the molecule. Finally, with the aid of special reagents he cleaves the large molecule at its vulnerable points, such as the double bonds. This process provides smaller organic molecules whose structures are usually known. This information, in conjunction with knowledge of the properties of the pigment, makes possible deduction of the molecular structure of the original compound just as fossil remains permit reconstruction of the appearance of prehistoric organisms.

As shown by chemical analysis molecules of most carotenes contain 40 atoms of carbon and 56 atoms of hydrogen. Molecules of most xanthophylls contain these same numbers of carbon and hydrogen atoms and from one to six or more atoms of oxygen in addition. These oxygen atoms render the xanthophylls relatively more soluble in alcohols than the carotenes.

From an analysis of their parts all xanthophylls and carotenes were found to contain a series of carbon atoms united by alternate single and double bonds. It is these alternate single and double bonds (the so-called conjugated double bonds) that are responsible for absorption of light by carotenoid molecules. The number and the arrangement of these double bonds determine the spectral absorption properties of the pigments. The larger the number of conjugated double bonds the greater the absorption. Changes in the spatial arrangements of the atoms near the double bonds account for the formation of the labile isomers of both xanthophylls and carotenes.

In molecules of some carotenes, as in the lycopene of tomatoes, the ends of the chain of carbon atoms are branched and contain only a few double bonds. These pigments are not converted to vitamin A in the animal body. In the molecules of other carotenes one or both ends of the chain may be coiled into rings of carbon atoms already familiar to the chemist as parts of the ionones, synthetic compounds having the odor of violets. Only those carotenes that contain a terminal ring identical with that in *beta*-ionone are converted into vitamin A by animals.

DIATOM PIGMENTS SEPARATED BY ABSORPTION UPON A COLUMN OF POWDERED SUGAR

Years of patient work in many different laboratories have demonstrated that the carbon skeleton of xanthophyll molecules is similar to that of the carotenes; hence, xanthophylls may be regarded as oxygen derivatives of carotenes. In many xanthophylls oxygen atoms occur as oxo (=C=O), as cyclic oxides, or as hydroxyl groups (≡C—OH) in both of the terminal rings referred to above. These pigments do not exhibit vitamin A activity. Other xanthophylls, by contrast, contain one ring free of oxygen atoms and exhibit pronounced vitamin A activity. A few carotenoids which contain acidic terminal carboxyl groups in place of the ring structures are not precursors of vitamin A.

Xanthophylls found in many of the yellow parts of

plants usually have their hydroxyl groups combined with fatty acids in the form of esters, whereas these same pigments found in the green plastids are unesterified. The solubility of these esters resembles that of the carotenes rather than that of the xanthophylls. Hydrolysis with alkali converts the esters into xanthophylls and salts of the fatty acids.

On the basis of chemical structure xanthophylls and carotenes are closely related to a portion of the green chlorophyll molecule and to vitamins E and K (both found in leaves) as well as to vitamin A (not found in plants). This suggests that all these compounds may originate in nature by similar mechanisms. It illustrates how chemical investigations may uncover new and unsuspected relationships between organic materials found in living organisms.

TECHNOLOGICAL IMPORTANCE OF CAROTENOIDS

Human populations, herds, and flocks now receive large amounts of processed preserved foods. The skilled technicians who regulate this complex food and fodder industry are paying increased attention to the importance of carotenoids in nutrition. Growth, resistance to disease, sensitive sight in weak light, and general good health in man, in animals, and in fowls depend upon an adequate supply of vitamin A or of carotene. High egg production by hens and quality milk and butterfat production by cows also hinge upon a liberal supply of carotene or vitamin A.

Because of increased demands for the limited supplies of natural, colorless vitamin A, its precursor, carotene, is being prepared on a large scale. For this purpose plant material of high carotene content is desired.

Alert farmers and plant breeders are selecting strains of plants that are rich in carotene. Both farmers and millers are working out methods for the preservation of the carotene contained in hay and in other dried fodder such as alfalfa meal. Food processors are devising preservation procedures that result in a minimum loss of carotene.

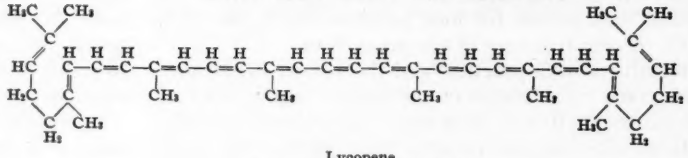
As consumers become more conscious of the value of the natural yellow constituents of foods, new demands for carotene-rich products will undoubtedly be made. Owing to their ready detection by the eye and because they deteriorate rapidly in improperly preserved plant material, carotenoid pigments are indicative of the nutritional quality of foods.

HOW DO CAROTENOIDS REACT IN LIVING ORGANISMS?

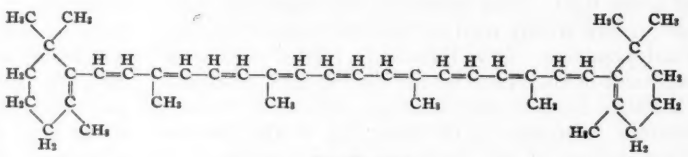
This story of the yellow fat-soluble pigments has been outlined by specialists in many different fields. Some of the chapters are nearing completion; others are but partially written; more shall certainly be added.

Over 100 carotenoid pigments have been discovered; many more probably exist. Most of the pigments have been obtained in a high state of purity; others have yet to be purified. Complete molecular structures of many

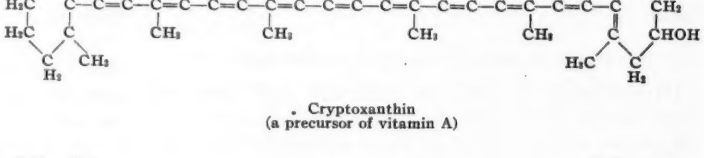
MOLECULAR STRUCTURES OF SOME CAROTENOID PIGMENTS



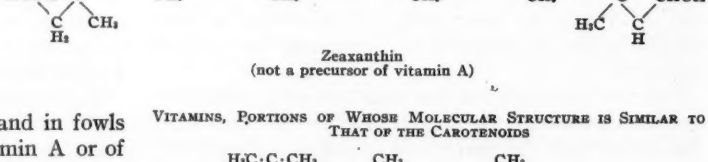
Lycopene
(not a precursor of vitamin A)



beta-Carotene
(a precursor of vitamin A)

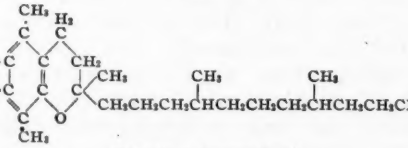


Cryptoxanthin
(a precursor of vitamin A)

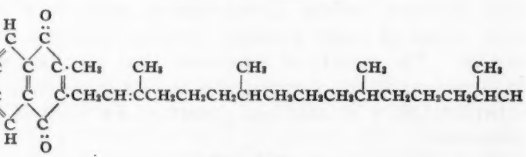


Zeaxanthin
(not a precursor of vitamin A)

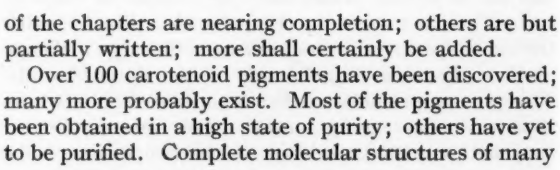
VITAMINS, PORTIONS OF WHOSE MOLECULAR STRUCTURE IS SIMILAR TO THAT OF THE CAROTENOIDS



Vitamin A



Vitamin E (α-tocopherol)



Vitamin K_1

have been established. Structures of others remain unknown.

Formation of carotenoids in plants is influenced by internal factors, such as heredity, and by numerous external conditions, such as light, temperature, oxygen, and nutrient salts. Plastids of fruits and flowers undergo marked physical and chemical changes as the chlorophylls disappear during formation of special yellow pigments; but the selective forces controlling synthesis of particular yellow pigments remain to be discovered. Specific functions, such as their role in photosynthesis, in vision, and in the formation of vitamin A, have been found for only a half-dozen or so xanthophylls and carotenes.

Scientists, having learned which carotenoids occur in different plants, are now seeking the precursors of the pigments—possibly small unsaturated molecules that may be condensed or large molecules that may be dehydrogenated. They are also hunting the chemical reactions by which animals convert carotenoids into other physiologically active substances.

These mysteries of the indispensable carotenoid pigments, begot by countless generations of plants and animals, are certain to be solved by the prying methods of modern research. New results of theoretical and practical import will accrue to the benefit of all mankind.

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Use of the Neon Bulb for Conductivity Demonstration

G. W. THIESSEN, *Monmouth College, Monmouth, Illinois*

THE use of the time-honored incandescent bulb in series with a pair of immersion electrodes for demonstration of electrical conductivities of solutions seems to be dropping out of favor. Arrangements using lecture galvanometers appear in some manuals. The galvanometer, of size and characteristics suitable for lecture demonstration, is a fairly expensive instrument, and its working is not so obvious to a group of beginning students as is the bulb; but it does give quantitative indication, and this is a real advantage. Thus, with the bulb demonstration distilled water does not light the bulb, nor does toluene, from which the student reasons that these two liquids are in the same class in point of polar properties. This idea is embarrassing later, when, in the study of pH of alkaline systems, the thought must be brought out that water has measurable ionization. A neon lamp of one-half watt rating will light perceptibly, for a large class, through laboratory distilled water, on which a 10-watt incandescent will, of course, not light. It will show no indication through toluene, pure or saturated with HCl, if the electrodes are reasonably dried from water (towel wiping, toluene rinse). It would be possible to cut in either bulb by a switch, but it is more impressive simply to change the bulbs in one socket. A rough index of the conductive power of the liquid under test with either bulb is afforded by having a metal conductor at hand to short-circuit the terminals of the conductivity cell. For safety, a screwdriver with an insulating handle is recommended for this purpose. If the glow of the light does not increase, it may be judged that the liquid under test is about as good a conductor as the excellently conducting metal rod.

The author has made his conductivity cell in the shape of a pair of dip electrodes from the carbon centers of small flashlight battery cells. Each has a stout wire soldered to its brass cap, which acts as a support. These are held in small bind posts on a bakelite strip. The strip in turn is supported by a small wood base. A handle is provided by which the entire setup may be lifted. The electrodes will dip into a 25-ml. beaker when the cell platform is set beside it. It thus is self-supporting, an advantage if bulbs must be changed.

It is intended that the bulbs be operated, as usual, from the conventional 110-volt alternating-current power lines. It should be kept in mind that a minimum voltage, in the neighborhood of 50, is required to operate a neon bulb.

Being rather insensitive to electric shock, the author sometimes demonstrates that sufficient current to light the neon can pass through his body; but he does not recommend this demonstration to others.

Considering the power voltage as rounded off to 100, the half-watt neon bulb is fully lighted on a current of 0.005 ampere, and the ten-watt filament lamp on 0.1 ampere. Half and quarter powers may be roughly judged and related to proportional currents. This gives about as close a reckoning of the amperage as is needed in first-year chemistry, if amperage figures are required in the record.

George Washington Carver

An American Scientist

CLARENCE W. WRIGHT

Livingstone College, Salisbury, North Carolina

INTRODUCTION

GEORGE Washington Carver, who appeared on the American scene around the middle of the nineteenth century, was a figure destined to give chemistry a new significance and interpretation. By means of botany, chemistry, and agriculture, this humble Afro-American was destined to point the way to better living and a more abundant life. He took the common things about him, and, by means of test tubes, retorts, and crucibles, made them quite uncommon. Yet, there has been some degree of doubt concerning Carver's discoveries in science; there has been a question in the minds of many scientists as to whether or not Carver should be classified as a scientist. However, such opinions may be due to a lack of serious study of his scientific contributions. Although numerous works have appeared on Carver and his contributions, few of these are based on reliable documented facts. Thus, it is the aim of this article to present a few facts gathered from available scientific literature which may aid in removing any doubts concerning Carver's contributions to science and serve to place him rightfully beside the other great scientists of his day.

EDUCATION

George Washington Carver (1864–1943), D.Sc., Ph.D., Director of Agricultural Research and Professor of Chemistry at Tuskegee Institute, Alabama, was born of slave parents in 1864 in a one-room cabin at Diamond Grove, Missouri. At the age of ten he was permitted by the Carvers, his white master and mistress whose name he bore, to attend a small school for the colored at Neosho, a village eight miles distant. Carver then followed up this early training by enrollment in a high school at Minneapolis, Kansas, where he was graduated. Then, in 1887, he applied to Simpson College at Winterset, Iowa, and was accepted. He studied there for three years, after which he applied for the second time to Iowa State College. This time he was admitted. He entered and received shortly thereafter the degree of Bachelor of Science. In 1896 he received the degree of Master of Science from the same institution.

During the latter part of this time he was placed in charge of work in systematic botany and bacteriology in the laboratories of Iowa State College. In 1895 Carver's name, along with the names of staff members, appeared in the *Iowa Agricultural State College Experiment Station Bulletin* as "assistant botanist." The same year his name appeared among the members of the Iowa Academy of Sciences as "associate member." He held this position at the Experiment Station until he met Dr. Booker T. Washington of Tuskegee Institute, Alabama, after which he became connected with the latter institution, a post he retained for more than 40 years, despite the fact that during this period of time he was offered positions with enormous salaries by Henry Ford, Thomas Edison, and several others.

CONTRIBUTIONS TO BOTANY

One of the earliest scientists of color to popularize negroes as scientists was George Washington Carver. It was mainly through his contributions that the negro received early recognition in science, and people everywhere became aware of the negro's ability in this field. Possibly Carver's earliest contribution to science was his investigations of the ferns.[1]

While on the staff of the Iowa Agricultural College Experiment Station, he became exceedingly interested in some of the problems of plant pathology. Through the inspiration and encouragement of Louis Herman Pammell, botanist, teacher, and friend, Carver set his hands to the task of solving some of these problems. After conducting experiments in plant pathology, Pammell and Carver published jointly in 1895 significant results on the prevention and cure of spot disease of currents and cherries, a method which consisted of treating the plants with "Bordeaux's Mixture."[2]

In the same year Carver published, again jointly with Pammell, another important study in plant pathology which appeared in the journal of the Iowa Academy of Sciences.[3]

Later that year, working with F. C. Stewart, Carver conducted special investigations on several species of parasites or bacteria which produced destructive diseases in cultivated plants. A study was made of the rust of wheat, oats, blackberry, and carnation. These studies, which proved to be significant, were also published by the Academy.[4] The following year, 1896, Carver published a paper setting forth his special experiments and methods in handling certain flowering plants.[5]

Other experiments dealt with the different types of soil, moisture, sunlight, rootage, rooting cutlings, and reproduction of plants. It is also interesting to note that on January 1, 1919, the Iowa Agricultural College Experiment Station published a "Complete List of Publications" in which the experimental works of Carver were listed.

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[5] CARVER, G. W., *Iowa State Coll. Agr. Expt. Sta. Bull., No. 32*, 516–26 (1896).

DISCOVERIES IN PLANT PATHOLOGY

A search into literature on plant pathology reveals that Carver made some very important discoveries in this field. In 1897 Carver reported for the first time a new species of *Taphrina*, a fungus found on red and silver maple trees. Anna E. Jenkins of the U. S. Bureau of Plant Industry, reporting on the taxonomic history of this fungus before the American Association for the Advancement of Science at Richmond in 1938, stated that a species of *Taphrina* was collected in Ontario several years earlier (July 17, 1893) by Dearness, who failed to recognize it as such until Carver had given a description of the same fungus which he found on several diseased leaves of silver maple at Tuskegee Institute.[6] This commentator further states: "Since Carver appears to have been the first to observe the asci of this species of *Taphrina*, it seems particularly fitting that it be named in his honor. It is therefore named *Taphrina carveri* . . . ."[7] Also according to Rackham Holt, other fungi were named in Carver's honor. Two of these were *Collectotrichum carveri* and *Metasphearia carveri*.[8]

Certain other facts show that Carver was the first to observe and report a fungus growth which caused a disease of the soybean. In 1910 Carver published an exhaustive study of *Cercospora* of Macon County, Alabama, in which he described for the first time in America *Cercospora canescens E and M*.[9]

Samuel G. Lehman, plant pathologist at the North Carolina Agricultural Experiment Station, stated the following in his exhaustive study on Frog-Eye leaf spot caused by *Cercospora diaza miura* which had attacked soybeans:

> Except for a few earlier and very brief statements regarding the occurrence of the disease herein described, there has appeared as yet in America no account of the active parasitic attack on soybeans by any fungus in the genus *Cercospora*. In 1901 Carver, in publishing a list of 75 species of *Cercosporæ* found in Macon County, Alabama, noted the occurrence of a fungus, which he designated *Cercospora canescens E and M*, on soybean and several other unrelated hosts. This appears to be the earliest reported occurrence of a *Cercospora* on soybean in America.[10]

However, Lehman was in error as to the date of Carver's discovery of *Cercospora canescens E and M*. The correct date was 1899. The original study of Carver's 60 or 75 different types of *Cercospora*, among which was listed *Cercospora canescens E and M* which attacked soybean, was reported in 1899. During this same year Carver reported on *Cercospora* to the Iowa Academy of Science.[11]

CONTRIBUTION TO AGRICULTURE

Shortly after Carver went to Tuskegee in 1896, he started the *Tuskegee Institute Experiment Station Bulletin* designed after that of Iowa State College. The *Tuskegee Bulletin* appeared quarterly from 1898 to 1936 in 42 editions. Each bulletin dealt with useful knowledge resulting from Carver's experimental findings. The first issue of the *Bulletin* appeared in February, 1898, and was sent gratis to those who desired it, especially farmers.[12]

Some of the studies published in the *Bulletin* were: "Feeding Acorns," *1*, 1898; "Some *Cercosporæ* of Macon County, Alabama," *4*, 1903; "Cow Peas," *5*, 1903; "How to Build Up Worn out Soil," *6*, 1905; "Cotton Growing on Sandy Upland Soil," *7*, 1905; "Successful Yields of Small Grains," *16*, 1909, etc.

CONTRIBUTIONS TO AGRICULTURAL CHEMISTRY

The information concerning Carver's contribution to chemistry provokes probably the most doubt as to his acceptance as a scientist; nevertheless, as time goes on, further research may prove him to have been as proficient in chemistry as in botany. In 1924 the *New York Times* carried the following editorial:

> It is for chemists to determine to what extent Dr. George Washington Carver of Tuskegee is worthy of recognition. Whether eminent or not, he seems to have done useful work in discovering and developing new uses for several common southern products, and therefore it can be claimed for him that he has shown abilities of a sort not present in many of his race. It is therefore to be regretted, and by none more than by the intelligent members of that race, that Dr. Carver, in discussing his own achievements, should use language that reveals a complete lack of scientific spirit.
>
> Real chemists, or at any rate, other real chemists, do not scorn books out of which they can learn what other chemists have done, and they do not ascribe their successes when they have any to "inspiration." Talk of that sort simply will bring ridicule on an admirable institution, and on the race for which it has done and still is doing so much.
>
> All who hear it will be inclined to doubt, perhaps unjustly, that Dr. Carver's chemistry is appreciably different from the astronomy of the once famous Rev. John Jasper, who so firmly maintained that the sun went around a flat earth.[13]

It is interesting to note that in 1930 Wade Moss, the Chemical Director of the Tom Hurston Peanut Company, Columbus, Georgia, in commenting upon an address delivered by Carver on creative chemistry, reported as follows:

> A year earlier, this address might not have been so successful, for then the South was not ready for creative chemistry. Now, the impetus has been given. It is being stimulated by the works of several men. Dr. Carver has blazed the trail.
>
> In this talk Dr. Carver stressed the fact he is a trail blazer. Having taken particular southern raw materials, he has demonstrated a variety of uses for each one. Some of them run into numbers. For instance the sweet potato yields to Dr. Carver's inventive genius and gives up 118 products. The peanut numbers perhaps 270, more or less.[14]

Wade Moss made another very significant statement concerning Carver's syntheses of organic dyes. He stated:

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[6] JENKINS, A. E., *J. Wash. Acad. Sci.*, **29**, 282 (1939).
[7] *Ibid.*, **29**, 229 (1939).
[8] HOLT, R., "George Washington Carver—An American Biography," Doubleday Doran & Company, New York, **1943**, pp. 200–1.
[9] CARVER, G. W., *Tuskegee Norm. Ind. Inst. Expt. Sta. Bull., No. 4*, 5 (1910).
[10] LEHMAN, S. G., *J. Agr. Research*, **36**, 811 (1928).
[11] CARVER, G. W., *Proc. Iowa Acad. Sci.*, **7**, 161–5 (1899).
[12] *Tuskegee Norm. Ind. Inst. Expt. Sta. Bull., No. 1* (1898).
[13] *New York Times*, Nov. 19, 1924.
[14] MOSS, W., *Mfrs. Record*, **98**, 58 (1930).

> The soils of Macon County have yielded to the great chemist's magic and given up many dyes and colors of gorgeousness and splendor. The blue, for instance, is made from red clay by oxidizing it intermittently for six successive operations, producing a color which is described as 70 times bluer than the bluest blue. Ten years ago, a church interior at Tuskegee was painted with this blue pigment made up into paint form, and in the passing years it has lost none of its gloss or sheen. No evidence of cracking or drying out appears. A scientist of distinction even has suggested that Dr. Carver has found a secret of the Egyptians.
>
> Through the method of preparation, this blue can be made for considerably less than any of the known blues, besides having the added advantage of being about 70 times richer than any other blue. The source of raw material is abundant. A steam shovel, a two-ton truck, and a simple factory complete a pigment plant. From rough calculations, it has been estimated that it could greatly undersell any pigment on the present market. Beyond this, its versatility appeals, as it can be used profitably in water colors or oil paints or as pigment in combination with minerals and plastics, with very few restrictions. This same blue when oxidized a few more times becomes royal purple.[15]

In conformity with the criteria suggested by the *New York Times*, Wade Moss has set Carver down as a "creative chemist" and in another work has referred to him as "the Wizard of Tuskegee." Christy Borth, another authority in chemistry, called Carver "the first and greatest chemurgist." Commenting upon Carver's work, he said:

> The first and greatest chemurgist is a negro whom race-proud southern whites have called "the saviour of the South." He is a scientist who was born a slave, a chemist most widely famed for more than 300 useful things which he extracted from the peanut.[16]

Carver is patentee of several of his methods used in discovering some of his products. As early as June 6, 1925, he patented cosmetics made from peanuts. On June 9 of the same year Carver received a blanket patent covering several processes for the manufacturing of paints and stains from clays and minerals. On June 14, 1927, he received a patent for an improved method of producing paints and stains, including the cold water processes.

For almost half a century Carver conducted research in agriculture, agricultural chemistry, and botany, and from the available literature it appears that his most monumental work was done in botany. His practical methods in agriculture and agricultural chemistry showed how much might be done with common farm products. He derived literally hundreds of products from such things as peanuts, sweet potatoes, cotton stalks, fibrous grasses and weeds, and waste materials of various kinds—dyes from the common clays of many states. He derived more than 200 products from the peanut and 60 products from the pecan. It is a question, however, whether or not each of these items discovered in chemistry was produced by chemical synthesis that may be used in the production of these items today. It seems highly improbable that the molecular structure, the atomic weights, the electronic behavior, and the physical and chemical laws governing the behavior of the chemical reactions of his many compounds or mixtures could be understood and recorded in such a short period of time by one man. If, however, time shall prove this to be the case, Carver will go down in the annals of history as one of the greatest scientists the world has ever known.

[15] *Ibid.*

[16] BORTH, C., "Pioneers of Plenty, Story of Chemurgy," The Dobbs-Merrill Company, Indianapolis and New York, 1939, p. 226.

SOME HONORS WELL EARNED

Dr. Carver received many honors for his tireless work in the field of science. Among the many was that given him when he spoke before the Ways and Means Committee of the House of Representatives on the peanut tariff. Carver was spokesman for the southern planters who wanted a tariff to protect themselves from the competition of the coolie and slave labor in foreign peanut industries. Each speaker was granted ten minutes in which to give his plea on the matter under discussion. Dr. Carver was the last to speak. As he spoke he exhibited his many products made from the peanut. When he had consumed the ten minutes allotted him, the majority of the legislators, who had listened attentively to his amazing story, called for him to continue. He spoke on and on, for one hour and 45 minutes. When he concluded, there was an outburst of applause and, needless to say, the peanut planters were protected. On another occasion, Dr. Carver spoke before the Texas State Senate and House of Representatives on the peanut.

In 1925 Iowa State College conferred upon Carver an honorary degree of Doctor of Science for his distinguished work in agricultural chemistry. Later that year, Simpson College likewise honored him with the honorary degree of Doctor of Philosophy. He became a Fellow of the Royal Society of Arts and Sciences of Great Britain, Spingarn Medalist for 1922, and recipient of the Roosevelt medal for achievements in chemistry in 1939. In June, 1941, Dr. Carver was awarded the honorary degree of Doctor of Science by the University of Rochester. Many schools have been erected in his honor. One of the Ford laboratories at Dearborn, Michigan, bears his name over its threshold. Not long before his death, Carver gave his life's savings, $30,000, to establish the George Washington Carver Research Foundation at Tuskegee Institute.

Carver's life with over half a century of service was brought to a close January 5, 1943. Though he is gone, his name will endure, and it is likely that the people of America, through their government, will erect a monument in honor of this great Afro-American's contribution to science and American progress and culture.

Invitation to Chemistry

WILLIAM J. WISWESSER

Willson Products, Inc.

Reading, Pennsylvania

R.S.V.P.

THE news of an "Atomic Era" in August, 1945, recalled these two-year old random notes on new horizons as seen in 1943 while teaching chemistry at Cooper Union, New York, N. Y. In view of the striking subsequent developments these comments and quotations have been brought up to date in the hope that they might serve as inspiration for all who are aware of the vital teaching tasks that lie ahead.

In less than a hundred years chemical knowledge has grown so fast and so powerful that it is now a major factor in the destiny of the human race—and it cannot be ignored. This growth was no surpise to some pioneer visionaries. As early as 1830 a Scottish scientist (*1*) put this final statement to his "History of Chemistry" in the final chapter entitled, "Of the present state in chemistry":

> Let the science advance for another century with the same rapidity that it has done during the last 50 years, and it will produce effects upon society of which the present race can form no adequate idea.

Perhaps Professor Thomson's prediction was a few decades premature, and certainly was not believed outside the circle of his own fellows. Most modern historians have ignored this *chemical* phase of civilization as faithfully as their predecessors ignored the little currents among the common people. For example, in the 800-page "Rise of American Civilization," written in 1927, the capable Beards (*2*) considered the impact* of chemistry on civilization so unimportant that it was dismissed in one single sentence:

> Having prefixed "industrial" to their title, chemists, whose forerunners once sought the philosopher's stone, now vied with one another in discovering new commercial substances or in turning old elements to novel uses in the manufacture of commodities, the increase of agricultural produce, or the destruction of diseases.

Perhaps that was all that the chemistry of 1927 deserved; it doesn't sound particularly flattering nor consistent with subsequent developments. Then in 1941 Britain's widely known J. G. Crowther (*3*) struck a new note in emphasizing "The Social Relations of Science." Feeling the new war agony of his country, he proceeded to prove that we needed a new glance at horizons:

> The present crisis of civilization shows that science is a determining factor in the destiny of mankind . . . . The chief characteristic of the present age is science . . . . Science in the modern sense is only about 300 to 400 years old. It arose about the same time as the Renaissance and the Reformation . . . brought into existence by the same social forces . . . .
>
> The scientists who have been contending that science has no social relations, is a purely individual activity outside politics, and arises solely from intellectual freedom, are playing into Hitler's hands. The study of the history of science and technology seems to show that the prosperous periods in human history are due less to efflorescences of wisdom and more to new inventions which for a time reduced the difficulty of the material conditions of life . . . .
>
> Partington has recently remarked " . . . in the study of the development of man no part is more significant, even if more neglected, than that concerned with the use of materials."

It is noteworthy to recall here that archaeologists, in describing the ascent of man, identify his cultural stages by the kinds of materials that mankind had mastered—Stone, Bronze, Iron, Coal. Since last Fall this classification seems to have been eclipsed by the one emphasizing Slave Power, Wind and Water Power, Fuel Power, and Atomic Power—with the new accent on energy as well as matter.

What has happened in America since 1900 was poignantly described by William Haynes (*4*) in his 1936 essays on "Men, Money, and Molecules":

> Within an incredibly short time the sciences have ceased to be a mysterious ritual of laws and formulas available only to the initiated. Their latest discovery is cocktail hour gossip, and Wall Street finances its application to industry. Their technical terms bristle not only in textbooks but in the newspaper; and they have come to replace the classics as the hallmark of an educated person. Indeed without a working knowledge of the natural sciences, one passes through this modern world deaf, dumb, and blind.
>
> Like the freshman when he learned that he had been talking English prose all his life, we are a little dismayed . . . . Our dependence upon chemistry is appalling.

It is so difficult to appreciate how recent *and how personal* this great impact of science is that witnesses to the change have to go to great lengths of proof. Mark Sullivan (*5*) has keenly described many of these

* "Impact" is the key word in a new popular magazine, *Science Illustrated*, which has appeared since this paper was submitted, long after these comments were written.

pertinent changes in his record of "Our Times," the first volume covering "The Turn of the Century":

Due chiefly to medical progress between 1900 and 1925, man was enriched in the thing he prizes most—his security of tenure on life, his defense against disease and death. The average age of the people who died in 1900 was 49 years; of those who died in 1925, 55 years .... At the beginning of 1900 it had not yet been proved that yellow fever is transmitted by a mosquito, typhus by a louse, bubonic plague by a flea .... It was not known that typhoid and cholera come from germs in unclean water and milk; these diseases were still the scourges they always had been. Insulin for diabetes, vaccination against typhoid, emetin for dysentery, adrenalin—all were still unknown. Antitoxin for diphtheria and the X-ray were only just coming into use. Ehrlich had not yet made those 606 patient experiments that resulted in the remedy for syphilis. Radium had not yet been used in the treatment of cancer ....

Man was enriched in the quantity of power brought to his service and in the lowered cost of this power .... The gasoline-engine is an instrumentality about which almost any superlative can be used .... In 1900 the average farmer had, as the only supplement to his own muscles, the power of two or three horses to carry on his work .... In 1900 there was but one generating station exceeding 5000 horse-power ....

Man was enriched—fabulously enriched—in his access to material goods—comforts, conveniences, luxuries. In 1900 the automobile was a dubious novelty. There were in all less than 8000 in the United States .... There were less than *ten* miles of concrete road .... There was but one telephone for each 66 people .. In 1900 it was recorded that the number of silk stockings sold in the United States was 12,572 pairs—a pair for one person to each 2000 of the population ....

Man was enriched in his knowledge of the surface of the earth. During this period both the North Pole and the South Pole were reached .... In 1900 the great Texas oil-fields were still undiscovered .... The Marconi wireless was unperfected .... The tungsten electric light was not yet made. In 1900 there were no oil-burning locomotives, no flotation process for recovering copper, no vacuum cleaners, no self-starter, no electric cookstoves or electric irons, no fireless cookers, no disc phonographs ...

Man was enriched in his knowledge of the universe. In one field of pure science, understanding of the nature of matter, the advances made between 1900 and 1925 were greater than the sum of all the advances made in all time before. "It sounds incredible, but nevertheless it is true, that science up to the close of the 19th century had no suspicion even of the original sources of natural energy."—Professor J. J. THOMSON, "Outline of Science."

Then in 1900 came Planck's quantum theory with its first explanation of the particle-wave nature of radiant energy. In 1905 came Einstein's relativity theory with its mass-energy interrelation, explaining the *material* source of intense radioactive or solar energies. In 1911–13 came Rutherford's and Bohr's theories of atomic structure. In 1923–27 came the bizarre wave mechanical theories that further welded the basic natures of matter and energy, thus pointing the way to recent theories of nuclear structure and nuclear fission. Finally in 1942–45 came man's fearful success in the creation of insidiously simmering atomic piles and sunbursts of atomic explosions. But there is hollow pride in the laying of the atomic bombs ....

Clement Wood, in his "Outline of Man's Knowledge," might have been speaking for 1946 instead of 1927 when he predicted and reflected as follows (*6*):

This cross-section of the world (after removing the cloaks of bias and prejudice) now looks hideous, weighted with immense bloody trouble for the future .... Any decade, even the present one, may witness another general martial conflagration over the whole European-American-Asian world, far more destructive than the last; for more terrible engines of war's destructiveness are invented constantly .... This may sound unduly pessimistic; the man who is an unrelieved optimist, in the state of the world today, is blind. The only salvation for mankind is effective world peace ....

It is knowledge that men—the vast majority of men—have lacked for so long. This lack of knowledge has stained every land and every sea-way with the spreading scarlet of spilt blood. *Lack of knowledge* has caused that strange self-mutilating trait of mankind, the organization of hatred, in the form of dreadful group rivalries and wars. Man has never organized love of fellowman with any effectiveness. This is the task of man's future; and only knowledge can lead into this ....

The object of society is to socialize man's achievements .... Achievements consist primarily in *knowledge*, in ways and methods that man has invented for doing things .... The individual's object is to live, in the fullest amplest sense; and he can do this best by gathering what facts he can about the universe, by arranging them logically, and by learning how to use them. Only knowledge can let a man or woman round into a developed human being.

The fact that this was written 19 years ago, yet rings so true today, suggests that we still are repeating the same mistakes of ignorance, of heavily costly lingering learning. Today, because the world at large has disregarded this cultural instruction, the thinking men find our nation facing a crisis that is almost indescribably horrible—horrible because the average man does not know what an atom is, cannot comprehend radiant energy, stubbornly does not *want* to believe the terrible truths about atomic bombs, and is hell-bent for having another war quick before our "new enemies" catch up with us. "Modern Man Is Obsolete" declared Norman Cousins in October, 1945, expanding a *Saturday Review* editorial (*7*):

The beginning of the Atomic Age has brought less hope than fear. It is a primitive fear, the fear of the unknown, the fear of forces man can neither channel nor comprehend. This fear is not new; in its classical form it is the fear of irrational death. But overnight it has become intensified, magnified. It has burst out of the subconscious and into the conscious, filling the mind with primordial apprehensions. It is thus that man stumbles fitfully into a new era of atomic energy for which he is as ill equipped to accept its potential blessings as he is to control its present dangers.

Dozens of apprehensively written articles and pamphlets and books have appeared since Hiroshima—many of them "satellites" of the incomparably detailed Smyth Report (*8*)—but still the people do not learn about the dangers, much less the fundamentals that explain the dangers. [Is this any wonder, though, when *not a single one of these new "scientifically authoritative" writings (9, 10, 11, 12, 13) shows a clear and correct modern picture of what atoms look like!* Even those few which "take a look" at the atom (*14, 15, 16*) show pictures that are about 20 years obsolete.]

Dr. Harold C. Urey, who correctly pictured the atom *in 1930* and was one of the scientists who directed the work on the atomic bomb, confessed, "I'm a Frightened Man" (*17*), at the beginning of this fearful year:

All the scientists I know are frightened—frightened for their

lives—and frightened for your life .... We are afraid of what politicians and diplomats may do with the atomic bomb .... I hear people talking about the possible use of the atomic bomb in war. As a scientist, I tell you: *there must never be another war* .... I have never heard—and you have never heard—any scientist say there is any scientific defense against the atomic bomb .... The mere presence of the bomb cannot be detected by any "magical" means, and it is of such size that it could fairly easily be smuggled in pieces from one country and assembled in another to await explosion at the touch of a distant radio control ....

The atomic bomb is entirely different from other bombs .... Thousands die within a fraction of a second. In the immediate area there is nothing left standing. There are no walls. They are vanished into dust and smoke. There are no wounded. There are not even bodies. At the center a fire many times hotter than any fire we have known has pulverized buildings and human bodies into nothingness .... A single atomic bomb has the effect not only of 20,000 tons of TNT, but in addition starts a fire of hurricane intensity .... The will to fight will not lengthen the life of an attacked city five minutes .... Panic might empty the remaining cities .... Bombs of the future will be equal to a million or two million tons of TNT .... † The safety of countries in the future, like our personal safety in cities, must rest on the *law and conscience of man*, backed by a vigilant world patrol .... Let us do some more thinking about *that next war which must never be* .... There is no secret. There is no defense. The bomb is essentially cheap ....

If you—the people—let things drift, ... we will eat fear, sleep fear, live in fear, and die in fear .... Ending this menace ... is the most important thing in the world today .... There is only one answer: *World Control* .... Our "defense" is Control ....

Think! Because we would not face the obvious, mankind allowed fascism to blast Europe. Now if we still refuse to learn the lesson of cooperation, it will be not Europe, but the world, which will lie in ruins .... The bomb is fused. The time is short. You must think fast. You must think straight.

That was in January. But still the people—you—have not listened, have not learned, have not acted. For the week of March 25 *Time* news magazine reported (*18*):

Some Americans have almost forgotten the atomic bomb. Some think of it as just another weapon and think that an atomic war will be just another war. This week such ostrich notions were rudely jolted. "One World or None" (*19*) ... is a calm, hair-raising warning of swiftly approaching disaster. Americans who would like to die a natural death can read it with profit .... "Destruction by air power," says General Arnold, "has become too cheap and easy .... The existence of civilization (is) subject to the good will and good sense of the men who control air power." ... Physicist Edward U. Condon says, "Sabotage ... is a fearful danger and an attractive possibility for an aggressor .... Twenty thousand tons of TNT can be kept under the counter of a candy store." Physicists Frederick Seitz ... and Hans Bethe ... believe that almost any industrial nation can start producing bombs in about five years .... Irving Langmuir ... thinks the Russians may do it in three years .... In a summing-up chapter Dr. Harold C. Urey describes ... the atomic armament race, which is now in progress, "... and the end will be deadly fear everywhere." To the scientists, the only solution is a world government strong enough to make war impossible .... "The problem has brought us to one of the great crises of history. The arms race must be stopped. There is not much time."

† According to Dr. J. R. Oppenheimer (*18*), one type is so stupendously destructive that it would be reserved for "very major targets such as greater New York." Thus an air fleet that could destroy a city in one hour with TNT now could destroy the most of a nation in the same time with atomic bombs.

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Soap and water applied to a new type of wall covering will remove almost any kind of dirt, grease, or other stain, including Junior's crayon marks. The result of nine years of laboratory research and ten months of field tests, the new wall material will be ready for the public by July.

The time is coming, too, when telephone users will dial their own long distance calls. Engineers have made good progress toward licking the many problems involved. For example, they have worked out an automatic device which will record who makes each call, to what person and city, for how long, and all other information needed by the telephone company to make out bills to its customers.

The BASIS of IMPROVED *Electronics*

DOUGLAS M. CONSIDINE
DONALD P. ECKMAN

Brown Instrument Company, Philadelphia, Pennsylvania

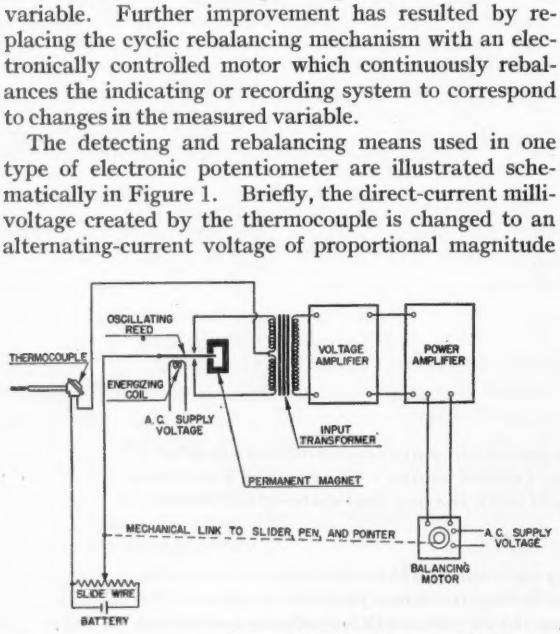
PROCESS instrumentation and chemical engineering have come a long way in the past decade. Consider for a moment how difficult it would be to conduct pilot plant developments or operate the great continuous processes of the chemical industry without precise, reliable measuring instruments which automatically and continuously indicate and record vital data. The industry's debt to instrumentation is high. Conversely, instrumentation is equally indebted to the industry because instruments are designed and developed to meet process needs. Instrumentation and processing are so interrelated and so interdependent that it would seem logical that instrumentation should be regarded by chemical engineers as a unit operation along with distillation, evaporation, crushing, and others.

Instrumentation has outgrown its swaddling clothes and no longer can be summarized in terms of mercury thermometers, pressure gages, flow meters, and the like. The utilization of electronic principles in industrial measurements has launched instrumentation into a new era.

ELECTRONIC POTENTIOMETERS

The increasing application of the self-balancing recording potentiometer to chemical processing has been brought about largely by the advent of basic improvements in the detecting and rebalancing mechanisms employed. One improvement is a direct result of using electrical means, other than the conventional galvanometer, for detecting changes in the measured variable. Further improvement has resulted by replacing the cyclic rebalancing mechanism with an electronically controlled motor which continuously rebalances the indicating or recording system to correspond to changes in the measured variable.

The detecting and rebalancing means used in one type of electronic potentiometer are illustrated schematically in Figure 1. Briefly, the direct-current millivoltage created by the thermocouple is changed to an alternating-current voltage of proportional magnitude



Courtesy of the Brown Instrument Company

FIGURE 1.—SCHEMATIC DIAGRAM OF ELECTRONIC POTENTIOMETER

in a converter. The converter is essentially a flat metal reed oscillating between two contacts connected to the opposite ends of the primary winding on an input transformer. The unbalanced direct-current voltage is impressed across the converter and the center tap of the primary winding on the input transformer. As the reed moves from one contact to the other, any unbalanced direct-current voltage will cause direct current to flow first in one direction through one-half the primary winding, then in the opposite direction through the other half. This action generates an alternating flux in the input transformer core, which in turn induces an alternating voltage on the transformer secondary.

The action of the converter is related to the alternating-current supply voltage by the energizing coil which is excited by the alternating-current supply voltage through a step-down transformer. The reed is polarized by a permanent magnet and, therefore, is actuated by the energizing coil to oscillate in synchronism with the a.-c. supply voltage. The reed closes one contact to the transformer for one-half the supply voltage cycle and the other contact for the other half, making one complete oscillation for each cycle. The direct current flowing in each half of the transformer primary winding, therefore, will create an alternating voltage in the transformer secondary of the same frequencey as the supply voltage. This alternating voltage is amplified in voltage and power to where it will actuate a two-phase balancing motor.

If there is an unbalance between the slide wire voltage and the thermocouple voltage, the balancing motor functions to rebalance the two voltages by moving the slider on the slide wire. The direction in which the motor turns is determined by a definite phase relationship between the a.-c. supply voltage and the amplified a.-c. thermocouple voltage. This relationship depends, of course, upon whether the measured variable is increasing or decreasing in magnitude.

This principle in potentiometric measurement has brought about higher speed of operation, greater sensitivity and accuracy of measurement, and better reproducibility. Consequently, research laboratory investigations, pilot plant operations, and processing in the chemical industry can be performed under closer supervision and control. In addition to temperature, such process variables as pH, high vacuum, spectrographic quantities, rotative speeds, and mechanical strain are particularly adaptable to measurement with this type of continuously balancing potentiometer.

Higher indicating and recording speeds, down to approximately four seconds across scale for many of these

instruments, have brought about the first really adequate means for measuring multiple temperatures. Instruments indicating with speed and precision as many as 48 separate temperatures permit scanning of a chemical unit operation as has never been done before. To plot data on a unit of operation where it is often necessary to know the temperatures at many intermediate points is but a matter of a few minutes. New processes are being aided in their development through the practicability of obtaining operating data quickly and efficiently.

Greater sensitivity of measurement has been accomplished through improvements in the rebalancing mechanism. In most cases, positive detection of changes as small as three-hundredths of one per cent of full scale is realized. On a pyrometer calibrated from 0 to 300°F., for example, this sensitivity will allow consistent measurement of changes in temperature as low as nine-hundredths of one degree.

The advantages of higher speeds of operation and greater sensitivity of measurement are multiplied in automatic control. It has been shown that in automatic control any increase in the speed of measurement will result in a considerable increase in the speed at which the measured variable will be returned to the desired value. This fact is true since the period of cycling of a process under control is about four times the total lag of the system. If this lag is reduced by employing a faster means of measurement, then the process will stabilize much more quickly.

The advantage of low measuring lag is easily noted in the automatic control of processes where the total lag is small, such as in the control of blower air temperatures. In some cases it has been found that if the measuring lag is reduced to a minimum by employing the newer electronic types of potentiometers, proportional or throttling control may be replaced by the simple type of on-off or two-position control.

On those processes which have a relatively large total lag or large heat capacity, such as heat exchangers, an instrument with a high sensitivity of measurement is of great advantage to automatic control. For example, in controlling temperatures associated with heat exchangers, changes in load and other unpredictable variations in processing cause the controlled temperature to deviate slowly from the desired value. The newer types of potentiometer controllers, which enable speedier response to small changes, apply a corrective action much sooner and reduce the deviation of temperature from the desired value.

The use of electronic and electro-mechanical components has virtually eliminated the multiplicity of moving mechanical parts common to previous potentiometers. Longer life is attained because of reduced wear on fewer moving parts. Reproducibility is also improved as a result of reduction in wear. The sturdiness and reliability of the electronic potentiometer has been proved in severe service. The absence of a delicate galvanometer movement and its associated mechanism make an instrument which, in many respects, is more powerful and rugged than the simplest pressure type thermometer.

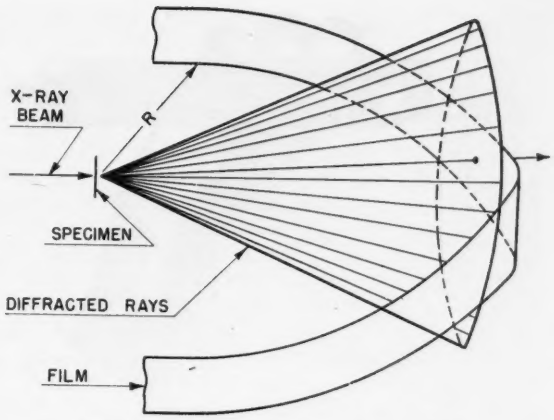


FIGURE 2.—FILM TYPE X-RAY SPECTROMETER

The cases which follow point to a few of many applications which either are rendered possible through use of the newer types of potentiometers, or which are increased considerably in their over-all usefulness.

GEIGER-COUNTER X-RAY SPECTROMETER

The use of X-ray diffraction by the chemical process industries as an analytical tool to determine the ultimate structure of materials has been employed for several years, for example, (1) in the rubber industry—to control the addition of dyes, fillers, and accelerators to the rubber batch—and (2) in the battery manufacturing industry—to select manganese dioxide ores required to impart specific battery characteristics and performance.

Until recently the time and technique required to perform and evaluate an analysis have limited the usefulness of this tool. The development of an X-ray spectrometer which greatly reduces the time required for analysis and which practically eliminates the need for special techniques in performing analyses is principally the result of two achievements in electronics—namely, (1) the Geiger-Müller tube, and (2) the continuously balanced high speed recording potentiometer.

When a finely collimated, essentially monochromatic beam of X-radiation bathes a properly prepared sample

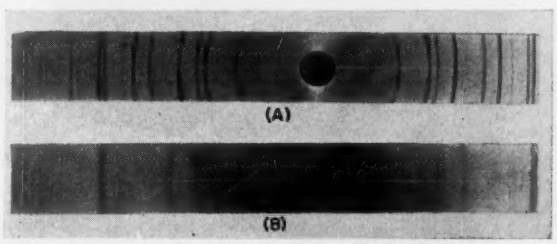
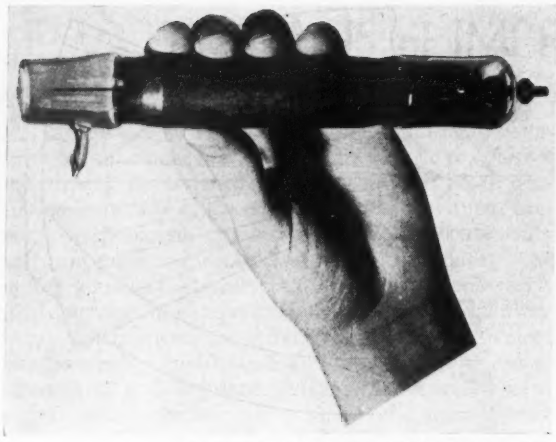


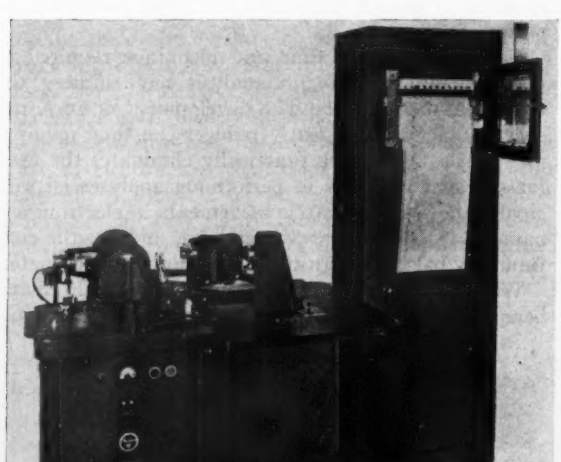
FIGURE 3.—DIFFRACTION FILM PATTERNS OF CATALYST SAMPLES
(*a*) Poor sample—sharp lines indicate grain growth and large particle size. (*b*) Good sample—film indicates small particles with large surface area.



Courtesy of North American Philips Company, Inc.

FIGURE 4.—GEIGER-MÜLLER TUBE

of material under test, a series of secondary reflected beams emerges. As illustrated in Figure 2, the secondary beams emerge from the sample in the form of a diffraction cone. By intercepting these beams with a strip of properly sensitized photographic film, a series of diffraction lines in the form of arcs of concentric circles is obtained (illustrated in Figure 3). The spacings of the lines are indicative of the materials that are present, and the densities of lines are indicative of the relative amounts of each material present in the sample. These lines occur wherever there is reinforcement of reflections from the surface and underlying atomic planes in the material. The phenomenon applies to all crystalline and to many amorphous substances. No two different materials have been found to exhibit the same diffraction pattern and hence identification by this means is positive.



Courtesy of the North American Philips Company, Inc.

FIGURE 5.—RECORDING X-RAY DIFFRACTION SPECTROMETER

With the photographic method considerable time is required (1) to set up the unit and prepare the film before exposure, (2) to expose the film (10 minutes minimum, 10 hours maximum), and (3) to develop the film after exposure. Once the film is developed, there remains a time-consuming manual task of measuring the line spacings and evaluating the line densities. Careful measurements and computations must be made to develop and to apply film shrinkage or extension factors since the film dimensions are affected during development. Likewise the density of the diffraction lines on the film versus the actual intensities of the reflected beams causing the lines is not a linear function, especially at the end zones. Integrity of results can be expected only for the middle ranges except through the adoption of rather involved time-consuming end-range techniques. It became obvious that improvements could be made on the photographic method.

The photographic film has been replaced by the Geiger-Müller tube, illustrated in Figure 4. This tube actually counts the quanta of X-ray energy reflected from the sample. The tube is prepared with close to 100 per cent efficiency for the characteristic X-ray wave length used in the spectrometer. In other words, one count is produced for almost every X-ray quantum entering the tube. It is interesting to compare this sensitivity with that of film which requires from 10^4 to 10^5 quanta to produce a diffraction line of minimum detectable darkness.

The Geiger-Müller tube is essentially a sealed tube containing an ionizable gas. Energy impinging on the tube causes partial ionization of the gas. The formation of a single ion pair anywhere within the active volume of the counter tube releases a flow of current sufficiently large to operate a relay directly. This current is amplified electronically over a range of 0 to 50 millivolts, which is fed to the high speed recording potentiometer illustrated in Figure 5. The recorder scale is evenly divided and is graduated from 0 to 100.

In the photographic method the strip of film is stationary. Where the counter tube is used, however, the tube is rotated about the sample so that it will scan the field of diffraction lines—that is, so that it will be progressively exposed to the various diffracted beams reflected from the sample.

Illustrated in Figure 6, the counter tube is rotated through 90 degrees of arc by means of a motor-driven scanning arm. This speed of rotation is precisely coordinated with the chart speed of the potentiometer to create an exact space relationship of the various intensity peaks and dips from the sample. Ninety minutes are required to obtain a complete diffraction pattern with the high-speed recorder. Where an automatic recorder is not used, it is necessary to position manually the scanning arm each 0.05 degree, requiring a total of 1800 positions.

FIGURE 6.—PARTIAL VIEW OF X-RAY SPECTROMETER

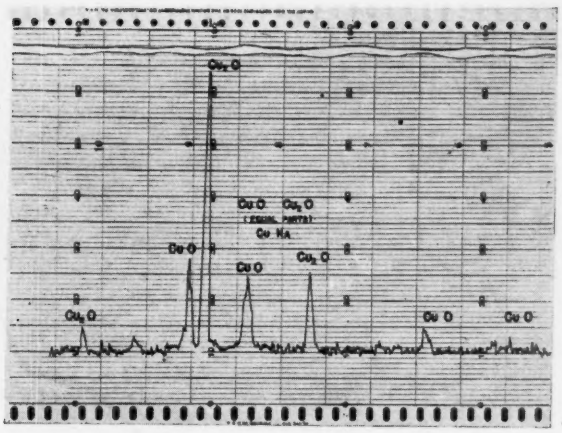


FIGURE 7.—TYPICAL X-RAY DIFFRACTION PATTERN OBTAINED WITH HIGH-SPEED RECORDING POTENTIOMETER

The type of pattern obtained with the electronic recorder is illustrated in Figure 7. This curve shows the proportions of cuprous and cupric oxides in a marine antifouling paint. The ratio of cuprous and cupric oxides must be held within close limits for optimum results, a difficult problem in the past. By use of the X-ray spectrometer, differentiation of the two products and determination of their relative proportions are easily effected.

The continuous high-speed operation of the recorder renders it possible to detect almost instantaneously the changes in the secondary radiation from the sample as the counter tube rotates. The fast pen speed of four and one-half seconds across scale and the high chart speed of 120 inches per hour make it possible to spread out the record, contributing to convenience and accuracy in analyzing the diffraction pattern.

THE RECORDING POLAROGRAPH

The Polarograph is an analytical instrument, both qualitative and quantitative, for determining the chemical constituents of either aqueous or nonaqueous solutions. Although extremely small quantities of material can be detected, it is not limited to micro analysis. Both in micro- and macro- analytical work, it replaces tedious and slow wet chemical methods for determining metallic and organic constituents.

The principle of the dropping mercury electrode, the basis of the Polarograph, dates back to 1873 when Lippman—using a capillary containing a stationary thread of mercury—first measured the surface tension of mercury successfully. Several years later Kucera—in making further studies of the surface tension of mercury—employed a dropping mercury electrode quite similar to the one now used in polarographic analysis. Kucera's method produced anomalous results which he could not explain nor eliminate from his experiments. In 1918 Heyrovsky—in attempting to find an explanation of Kucera's results—continued the investigation of electrocapillarity. A galvanometer was employed to measure the currents flowing through the electrode system, and it was discovered that the current-voltage curves of solutions which were electrolyzed with a dropping mercury electrode possessed several remarkable qualities, including: (1) the curves had a characteristic step formation, (2) the curves were a function of the nature of the solution and were reproducible, (3) the voltages at which the steps of the curves occurred were characteristics of the components in the reducible substance, permitting qualitative analysis, and (4) the height of the steps was a function of the concentration of the components of the substance in solution, thereby making quantitative analysis possible. The method of analysis was named polarography; the instrument developed by Heyrovsky was called the Polarograph; and the current-voltage curve was termed Polarogram.

The dropping mercury electrode, illustrated schematically in Figure 8, comprises a very fine bore capillary tube connected by a neoprene tube to a mercury reservoir and placed in the solution so that very fine drops of mercury are formed beneath the surface. The rate of mercury flow may be adjusted by varying the height of the mercury reservoir and normally

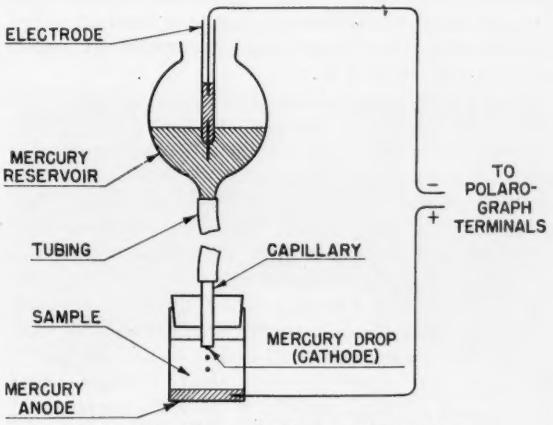


FIGURE 8.—DROPPING MERCURY ELECTRODE

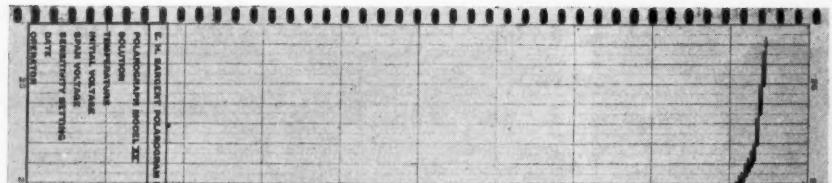


FIGURE 9.—POLAROGRAM OF COPPER, LEAD, AND CADMIUM IN A HIGH-PURITY, ZINC-BASE, DIE-CAST ALLOY

amounts to a drop every one to three seconds. The mercury reservoir is connected to one terminal of the Polarograph; the other cell terminal is a pool of mercury in the bottom of the solution vessel.

In operation a few drops of mercury added to the sample act as one electrode of the cell. The dropping mercury electrode is next inserted. An inert gas, usually nitrogen, is then bubbled through the solution to remove atmospheric oxygen which is reducible and gives a polarographic wave not usually of interest to the analyst. As the voltage impressed on the cell is slowly raised, the current remains nearly constant until a voltage is reached at which a component of the solution is reducible. The current then rises sharply to a new level at which it remains constant until the voltage is reached at which a second component is reducible. Another sharp rise in current to a new constant value then occurs. These sharp rises in current are called polarographic steps or waves.

Since the polarographic steps for the various components in the sample occur at different voltages, several substances may be determined in one solution on a single polarogram, as illustrated in Figure 9. Note the small percentages of copper, lead, and cadmium determined in a high-purity, zinc-base, die-cast alloy.

During his early experiments Heyrovsky found that manual plotting of polarograms was laborious and subject to experimental error. An automatic instrument was needed with the following characteristics: (1) continuous operation to show all details of the curves, (2) fast operation since current-voltage changes occur rapidly, and (3) high sensitivity since the currents involved are often fractions of a microampere.

A photographic recorder was developed which partially answered the needs. Although a great improvement, photographic recording, as in the case of X-ray diffraction previously described,[1] had many limitations, including: (1) time and labor required for photographic development of polarograms was considerable; (2) current-voltage curves were not visible while the analysis was being made. Visible chart recording permits prompt readjustment of operation conditions at any stage in the process of the polarograms; (3) precision was limited by the size of the record produced. With a strip chart record 12 inches wide, step heights of polarograms can be made very large, permitting greater accuracy in analyzing results. The ruled chart also simplifies the linear measurements required. By employing a continuously balanced high-speed recording potentiometer the above limitations

Courtesy of E. H. Sargent and Company

FIGURE 10.—HIGH-SPEED VISIBLE RECORDING POLAROGRAPH

have been overcome. The new unit is illustrated in Figure 10.

The output from the polarographic cell is fed to the recorder so that the displacement of the pen from zero is determined by the amount of current flowing through the cell. The chart is driven by a constant speed synchronous motor. The polarographic bridge which supplies voltage to the cell is also driven by a synchronous motor so that the chart displacement is a linear function of the voltage applied to the cell—that is, the time ordinate of the chart becomes, in essence, the voltage ordinate. The record obtained, therefore, is current versus voltage. Since the recorder pen is continuously visible, the operator is in position to determine when a step is completed and to make immediate readjustments if the curve is too small or too large.

Examples of practical applications of the Polarograph to process control include (1) the determination of carryover of aluminum chloride catalyst in petroleum processing, and (2) the indication of residual oxides of nitrogen in high explosives.

ULTRAVIOLET AND INFRARED SPECTROPHOTOMETERS

Spectrophotometry is based upon the fact that various chemical substances, in either the gas, liquid, or solid form, absorb light at certain wave lengths. When light of a single color or wave length is passed through a layer of any substance, the light may be transmitted completely through the substance, or it may be partially or completely absorbed, depending upon the chemical identity of the substance and the amount of the substance in the path of the light.

If a plot is made of wave length versus percentage of light absorbed under various conditions an irregular curve of hills and valleys will result. The hills correspond to wave lengths or colors for which the substance is relatively opaque; the valleys correspond to wave lengths for which the substance is relatively transparent. In some cases the hills show sharp absorption peaks; in other cases the absorption maxima are broad.

The absorption curve for any substance is unique. No two chemical substances absorb light in exactly the same fashion. The absorption spectrum of a substance serves as a fingerprint to identify the substance when in pure form. When the substance is mixed with another, usually it will be found that at least some of the absorption peaks of the substance will not coincide with the absorption peaks of other substances.

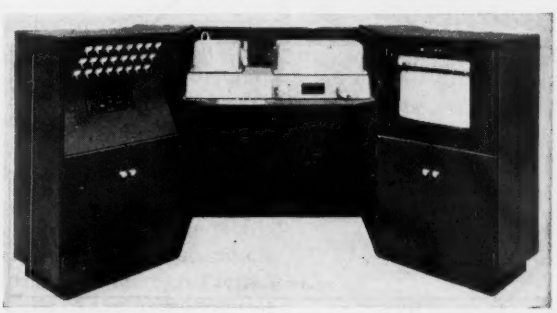
Substances which appear colored to the eye obviously absorb light in the visible region of the spectrum. Bromine vapors and copper sulfate solutions are common examples. Many chemical substances, particularly organic compounds, are colorless—that is, they are transparent for all wave lengths in the visible regions. Such substances will nevertheless absorb radiation in invisible spectral regions, depending upon the types of chemical bonds in the molecules. Thus molecules which include the benzene ring in their structure, such as benzene, toluene, and xylene, show distinctive absorption patterns in the ultraviolet region. Conjugated diolefins, of which butadiene is the most familiar example, also absorb in the ultraviolet region. Ordinary saturated hydrocarbons, such as propane and butane, and simple unsaturated compounds, such as butylenes, do not absorb extensively in the ultraviolet. For the analysis of such compounds the infrared region of the spectrum is utilized.

Ultraviolet Spectrophotometer: As illustrated in Figure 11, this instrument comprises (1) a source of ultraviolet radiation, usually a hydrogen lamp, (2) a monochromator to isolate radiation of any desired wave lengths, (3) an absorption cell through which a stream of the fluid being measured is continuously passed, (4) a phototube and electronic amplifier for measuring the amount of radiation transmitted through the sample, and (5) an electronic potentiometer which records the percentage of light transmitted by the sample. Chart readings of less than 100 per cent will be produced whenever the sample stream absorbs some of the radiation. By employing suitable calibration data, the per cent transmission can be correlated with the concentration of the measured substance in the fluid stream.

Infrared Spectrophotometer: In the infrared spectrophotometer, illustrated in Figure 12, a globar is used as the source of infrared radiation. Radiation from the globar is focused through a sample cell. Radiation transmitted by the sample cell is dispersed by means of a prism, usually made of rocksalt. By rotating a Littrow mirror, upon which radiation from the dis-

Courtesy of the National Technical Laboratories

FIGURE 11.—RECORDING ULTRAVIOLET SPECTROPHOTOMETER



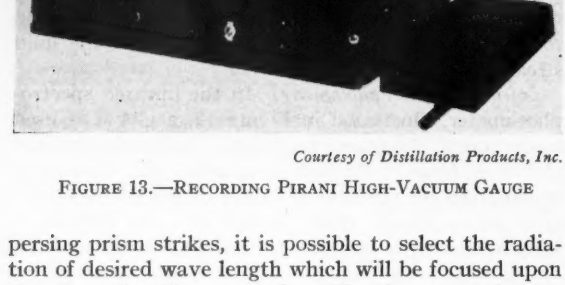
Courtesy of the Perkin-Elmer Corporation

FIGURE 12.—HIGH-SPEED RECORDING INFRARED SPECTROMETER

Courtesy of Distillation Products, Inc.

FIGURE 13.—RECORDING PIRANI HIGH-VACUUM GAUGE

persing prism strikes, it is possible to select the radiation of desired wave length which will be focused upon the measuring thermocouple. The thermocouple is a high vacuum compensated type with a bismuth-bismuth tin hot junction. The e. m. f. generated by the thermocouple is on the order of one micronvolt. The amount of energy for a given wave length picked up by the thermocouple is a function of the amount of radiation of that wave length absorbed by the sample.



Courtesy of Distillation Products, Inc.

FIGURE 14.—PIRANI CIRCUIT

By carefully rotating the micrometer wave-length control, which rotates the Littrow mirror, the complete infrared spectrum of the sample—from about 2.5 to 15 microns—is obtained. For automatic scanning of the spectrum where a high speed recording potentiometer is employed, the shaft of the wave-length micrometer is coupled to an electric motor drive. The thermocouple e. m. f. is amplified and recorded on a high-speed strip chart electronic potentiometer.

Advantages of continuously and automatically indicating and recording ultraviolet and infrared spectra include (1) a substantial reduction in the time and skill required to perform analyses is effected, (2) a permanent record is obtained which may be consulted for reference at any time, and (3) unknown absorption in samples often can be identified at a later date in the light of subsequent work, providing a permanent record is at hand.

MEASURING HIGH VACUUMS

Until recently an absolute pressure of 40 to 50 millimeters of mercury was considered a high vacuum. With exception of the manufacture of vacuum tubes, high vacuum techniques were generally confined to the laboratory. Today absolute pressures in the low millimeter and micron ranges are becoming commonplace and are making practical many processes formerly impossible to carry out and are improving the performance of many products.

Some processes in which high vacuums are now being applied include: (1) evaporation of metals and metallic salts, as in the manufacture of magnesium, surface plating of optical lenses, and metallic plating of cellophane; (2) drying blood plasma, penicillin, and other biologicals by sublimation; (3) distillation of vitamin oils, essential oils, and aromatics; (4) extraction of foods and drugs and the recovery of volatile solvents; (5) impregnation of coils, condensers, cables, armature windings, textiles, and wood; (6) manufacture of sealed unit refrigeration systems. The efficiency of the unit with removal of the last traces of water vapor and noncondensable gases is greatly increased; and (7) low temperature drying of foods and chemicals.

Continuous measurement of vacuums is indispensable to these processes because of the following reasons: (1) certain processes become inoperative if the pressure becomes too high. Continuous pressure measurement will indicate when the vacuum is more or less than that desired; (2) in certain processes there is a critical point at which undesirable effects will occur, if the pressures become too low. For example, arcing occurs in electronic drying if the pressures become too low; (3) leaks in vacuum equipment will be recorded by the pressure gage and an alarm will be set to give warning before damage occurs, such as melting in freeze-drying processes.

High-vacuum measurement roughly falls into three broad ranges—namely, 0 to 5000 microns, 0 to 500 microns, and 0 to 50 microns. Two types of high vacuum recorders are discussed in this paper—namely, (1) the Pirani Gauge, and (2) the McLeod Gauge.

Recording Pirani Gauge: The Pirani Gauge, illustrated in Figure 13, is essentially a coil of resistance wire mounted in an envelope which is connected to the system whose pressure is to be measured. The gage is connected into a Wheatstone bridge as one of the four arms. A second gage is usually sealed off at a pressure considerably lower than one micron of mercury, is connected to the bridge as a second arm, and is so arranged that changes in its resistance will balance changes in the gage tube resistance due to temperature fluctuations but not due to pressure changes. The remaining two arms of the bridge are equal fixed resistances. The measuring circuit is illustrated in Figure 14.

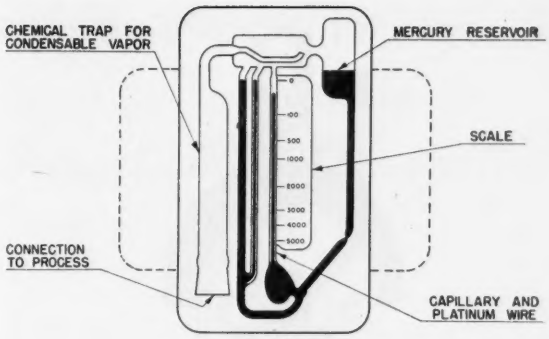
The heat loss from the filament of the gage tube, in pressure range from atmospheric pressure in one millimeter of mercury, is very largely due to convection and conduction. Below one micron of mercury the major heat loss is due to radiation and conduction. Between the pressures of one millimeter and one micron of mercury there is a considerable change in the heat loss from the filament due to the sharp change in the convection loss in this region, which causes its temperature to rise and this, in turn, causes its resistance to change and unbalances the bridge. This unbalance results in a current flow through the indicating arm of the bridge. A resistance placed in this arm will have an IR drop developed across it during unbalance which may be used to actuate a recording potentiometer. The potentiometer may be calibrated directly in terms of the pressure in microns.

The balance point of the gage, shown in Figure 14, is taken as the pressure of the sealed-off comparison tube, which means that the sensitivity is greatest at the low pressure end of the scale and least at the upper end of the scale. In the range of one micron a change in pressure as little as one-quarter micron may be observed, while at 500 microns a change of 10 to 25 microns may be the minimum change observable with accuracy. This change in sensitivity is due in part to the nonlinearity of the scale. The accuracy of calibration is of the order of ± 1 to 2 microns at the low pressure end, ± 10 to 15 microns at the high pressure end of the scale.

The pen of the potentiometer travels across scale in about 4.5 seconds so that even wide variations in pressure are almost instantly recorded. Contacts in the potentiometer recorder may be used for actuating alarm signals or even control circuits. Special sequence programs to fit particular applications may also be worked out with the potentiometer.

Recording McLeod Gauge: The McLeod Gauge after 70 years is still the ultimate standard for vacuum measurement and is used in the calibration of other vacuum gages. Noncondensable gases, such as hydrogen, cause no error in readings as with other types of vacuum gages. Condensable vapors, such as water or alcohol, can cause errors unless they are removed by a chemical trop or other means before they reach the measuring chamber of the gage.

The Stokes McLeod Gauge (Flosdorf-Hall) Type, illustrated in Figure 15, is now available for both measuring and recording high vacuums. Measurement is automatically made and recorded at regular intervals so that substantially a continuous record is obtained.



Courtesy of the F. J. Stokes Machine Company

FIGURE 15.—MCLEOD TYPE VACUUM GAUGE

In Figure 15 the gage is illustrated in its measuring position. The gage is turned periodically, as shown dotted, each cycle to permit the measuring chamber to be exposed again to the pressure of the process. The height to which mercury rises in the capillary of the measuring chamber is determined, of course, by the pressure in that chamber. This height is electrically indicated.

To reduce the sampling-measuring cycle of the gage, advantage of a high-speed electronic recording potentiometer may be taken. The steplike action of a galvanometer-type potentiometer limits somewhat the speed with which the complete cycle can be made, as sufficient time must be allowed for the galvanometer to come to balance on the measuring end of the cycle.

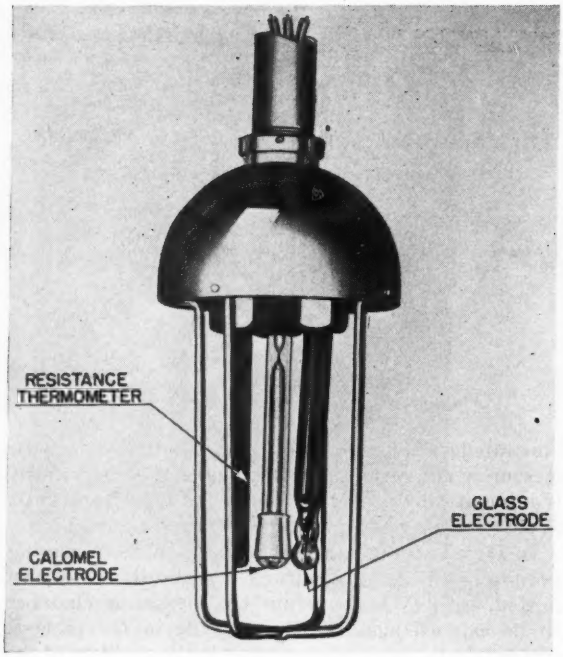
Ultra-High Vacuums: For pressures lower than one micron of mercury, the ionization gage, with a range of 1 micron to 0.001 micron, and the Philip's Gauge, with a range of 20 microns to 0.01 micron, also can be adapted for use with recording potentiometers.

Courtesy of National Technical Laboratories

FIGURE 16.—FLOW TYPE PH ELECTRODE ASSEMBLY

REFINEMENTS IN PH MEASUREMENT

Hydrogen ion concentration has been measured successfully in the laboratory for many years. The adoption of early laboratory measuring means to continuous indication and automatic recording and controlling of pH in industrial processes was not so successful. The industrial limitations of the hydrogen electrode, which requires a platinum catalytic surface



Courtesy of the National Technical Laboratories

FIGURE 17.—IMMERSION TYPE pH ELECTRODE ASSEMBLY

and a pure supply of hydrogen gas, included (1) susceptibility of the catalyst to poisoning and (2) requirements for a continuous supply of pure hydrogen gas. Quinhydrone and antimony measuring electrodes offered some improvement for certain industrial applications, but these were (1) generally subject to errors in oxidizing and reducing solutions and (2) susceptible to poisoning by certain ions and salts.

Development of the glass electrode several years ago was the first real step toward industrial pH measuring and controlling applications. These first electrodes were not the complete answer, however. Considerable research into various types of glasses and into the measuring circuits was necessary before many of the shortcomings of the early glass electrodes could be overcome. The shortcomings included (1) limitation of the electrode to relatively low temperatures, (2) effect of alkaline salts, especially sodium ions, above a pH of 9, (3) fragile construction which made careful handling manadatory, and (4) effects of changing humidity and stray currents upon the measuring system.

As a result of research during the past five years, the situation has been changed to the effect that (1) continuous pH measurements can be made in boiling aqueous solutions, (2) accurate measurement in highly alkaline solutions containing sodium ion concentrations of two mols per liter and up to a pH of 12 is obtainable, (3) delicate handling of the electrodes is no longer required, and (4) by improving the electronic measuring circuit and shielding the electrode leads, the effects of stray currents have been practically eliminated. It is not claimed, of course, that the ultimate in pH measurement has been reached, but recent progress has made industrial pH measurement and control possible where heretofore practical considerations seriously limited the applications.

Sturdy construction of electrode assemblies has also been responsible for a wider industrial usage of pH measurement. The flow assembly, illustrated in Figure 16, can be installed directly in process pipelines. Numerous materials of construction, including porcelain-covered iron, rubber, stainless steel, Monel metal, and Pyrex glass, can be used to fabricate the chamber. The immersion assembly, illustrated in Figure 17, is designed for permanent installation in tanks, vats, and other process vessels and is capable of operating under pressures of 30 pounds per square inch and over. In this assembly, note the three major parts—namely, the glass electrode, the calomel reference electrode, and the resistance thermometer. The resistance thermometer automatically and continuously compensates for the effects of temperature upon the resistance of the glass in the electrode.

Numerous special electrodes have been developed to satisfy peculiar process conditions. For example, an electrode assembly has been designed which does not expose any metal parts to the process solution. The production of penicillin requires a special electrode which permits the convenient measurement of pH of two liquid layers, a water layer, and a chloroform layer. pH measurement is important since it greatly affects the mutual solubilities of the liquids involved.

While the saturated calomel cell is generally used as the reference electrode, special mercury-less electrodes are available for processes, such as photographic film manufacture, where mercury cannot be tolerated.

In a lecture recently given by Sir Arthur Eddington in Chicago he said, "Never believe an experiment until it is checked by theory."

We may be sure that Sir Arthur could not have meant that we must go back to the Middle Ages when churchmen and philosophers would pay no attention to experiments or observations which did not accord with their cherished beliefs; nor can we think that the eminent astronomer would approve of those Fundamentalists and extreme materialists, Christian Scientists and physicians, antivivisectionists and biologists, economists and advocates of the New Deal, Marxists and Christian Socialists, Communists and capitalists, Democrats and Republicans, pacifists and big navy men, internationalists and Daughters of the Revolution, who are unwilling to advance by hypothesis, observation, and experiment. Very many in each of these classes are, of course, willing to use scientific methods and many shift from one group to the other for sufficient reasons.

From other things in his lecture we think he meant that random experiments and accidental observations are of little value unless they are guided by some fundamental principle which will help to explain them. In other words, experiment and theory must go forward together, and each must be constantly checked by the other.—W. A. Noyes

The Chemistry of Benzene Hexachloride and its Insecticidal Properties

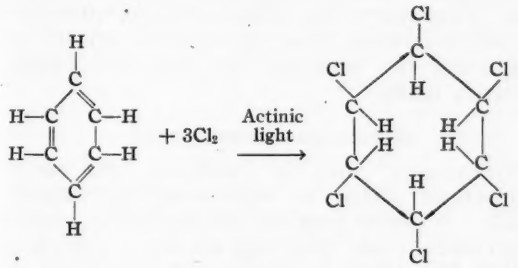
$C_6H_6Cl_6$

GEORGE R. CHAMLIN

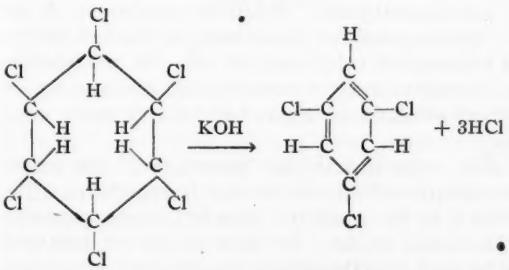
Continental Laboratories, Chicago, Illinois

A NEW insecticide—benzene hexachloride or 1,2,3,4,-5,6-hexachlorocyclohexane, called "666" for short from its empirical formula $C_6H_6Cl_6$—has been reported in British journals and by the U. S. Department of Agriculture[1] as possessing outstanding insecticidal properties.

Benzene hexachloride was first made in 1825 by Michael Faraday, who found that benzene reacted with chlorine in sunlight to give a solid body and a dense thick fluid:



In 1833 Mitscherlich described its decomposition by bases to form trichlorobenzene:



Peligot and Lauret established its composition in 1836, and in 1912 Van der Linden[2] the existence of four isomers. Pure specimens of alpha and beta isomers of "666" were prepared by J. C. Smart in 1942, and their toxocity to insects was investigated by F. J. D. Thomas at Hawthorndale, England. It was found that both isomers were practically nontoxic to insect pests. It was soon shown, however, that the insecticidal action of "666" was due almost entirely to the presence of the gamma isomer which was called "Gammexane." It is present to the extent of 10 to 12 per cent in the crude material.

COMMERCIAL PREPARATION OF BENZENE HEXACHLORIDE[3]

Chlorine gas is slowly passed into 660 parts of benzene contained in a lead-lined reaction vessel until 890 parts of the gas have been absorbed. The mixture is then stirred continuously and the temperature maintained at 15° to 20° C. in the presence of actinic radiations. The supply of chlorine is then interrupted, and the precipitated solid filtered off and dried. The mother liquid is then mixed with 330 parts of benzene and the mixture again treated with 890 parts of chlorine. After filtering the reaction mixture resulting from the second chlorination, the filtrate is again mixed with a smaller quanity of benzene and again chlorinated in a similar manner. In this way, a continuous process for the preparation of benzene hexachloride results.

SEPARATION OF THE PURE GAMMA ISOMER

The crude $C_6H_6Cl_6$ is treated with a small amount of methanol, in which the alpha and beta isomers are relatively insoluble. Separation of the solid product leaves a solution containing the gamma and delta isomers. On evaporating the solution, a small crop of practically pure gamma isomer is thrown down. This can be recrystallized from $CHCl_3$ or hot concentrated HNO_3.

According to Dr. Donald Slade (Imperial Chemical Industries, Ltd.), there are probably 16 possible configurations for benzene hexachloride. In view of the strain produced by the close approach of chlorine atoms (this can readily be seen from atomic scale models) he suggests that there are only five probable strainless forms of $C_6H_6Cl_6$, two of which are mirror images. Of the five formed, the structure of beta isomer is the only one whose structure is known with certainty.

PROPERTIES

The benzene hexachlorides are stable compounds which are unaffected by continuous exposure to the atmosphere. They are stable to the action of hot water and light for a considerable period. They can be recrystallized from hot concentrated HNO_3. In the presence of alkalies, such as limewater at ordinary temperatures, three molecules of HCl are lost from the

[1] Report entitled "The New Insecticide Benzene Hexachloride (666)" by the Bureau of Entomology and Plant Quarantine, Beltsville, Maryland.

[2] *Ber.*, **45**, 236 (1912).

[3] United States patent 2,218,148.

$C_6H_6Cl_6$ molecule giving a mixture of the isomers of trichlorobenzene. The beta isomer is the most stable, being less reactive to dilute alkalies than the other isomers.

In the pure state the isomers of benzene hexachloride are well-defined colorless crystals, relatively insoluble in H_2O, soluble in organic solvents, practically odorless, and having a bitter taste. The melting points of the alpha, beta, gamma, and delta forms are, respectively, 158°, 309°, 112.5°, and 138.5°C. A list of solubilities appears in Table 1. The consistently low solubility of the beta isomer and also the higher relative solubilities of the gamma and delta isomers are to be noted.

TABLE 1

SOLUBILITIES OF ISOMERS OF BENZENE HEXACHLORIDE AT 20° C. IN COMMON SOLVENTS

Solvents	*Solubility, g./100 g. solution*			
	Alpha	*Beta*	*Gamma*	*Delta*
Acetone	13.9	10.3	43.5	71.1
Benzene	9.9	1.9	28.9	41.1
Carbon tetrachloride	1.8	0.3	6.7	3.6
Chloroform	6.3	0.3	24.0	13.7
Cyclohexanone	17.3	12.1	36.7	49.9
Diesel oil	1.5	0.3	4.1	9.2
Dioxan	33.6	7.8	31.4	58.9
Ether	6.2	1.8	20.8	35.4
Ethyl alcohol	1.8	1.1	6.4	24.2
Ethyl acetate	12.7	6.9	35.7	58.5
Ethylene glycol	0.3	0.1	0.6	4.1
Glycerin	0.02	Nil	0.06	0.2
Methyl acetate	13.6	6.7	27.7	62.1
Methyl alcohol	2.3	1.6	7.4	27.3
Naphtha (heavy)	5.8	1.5	18.1	30.4
Iso-propyl alcohol	0.6	0.4	2.8	18.0
Toluene	9.0	2.1	27.6	41.6
Distilled water (parts per million)	(10)	(5)	(10)	(10)
Xylene	8.5	3.3	24.7	42.1

INSECTICIDAL EVALUATION OF "GAMMEXANE"

Tests, still in progress conducted in our laboratories and in the field, indicate that "gammexane" is highly toxic to many insects.

Periplaneta americana (*the American cockroach*): "Gammexane" mixed with bait (1 to 500) was fed for 10 days to 100 cockroaches (10 in each of 10 jars), all but 3 of which died. In other tests one per cent of "gammexane" in talc was applied on a band one inch wide across the center of a pen 20 inches square; all the adult roaches exposed were killed within 20 hours. Concentrations as low as 0.002 per cent were completely effective in 104 hours. When 10 per cent DDT (dichloro-diphenyl-trichloroethane) and 97 per cent sodium fluoride were compared with "gammexane," only 60 per cent of those roaches treated with DDT and 50 per cent of those with sodium fluoride were dead at the end of 48 hours.

In a practical test in a restaurant a spray containing one per cent "gammexane" was applied to the surrounding surfaces. Twenty-four hours later 624 dead and dying cockroaches were counted, and two weeks later the premises were completely free of insects.[4]

Cimex lectularius (*the bedbug*): In order to simulate natural conditions, cages containing miniature mattresses were used. Spray was applied to the mattresses and to the lower half of the cages at the rate of 20 mg. per sq. ft. of surface. Fresh bedbugs were introduced weekly. Mortality in these cages was complete after 90 days.

In several small tests in rooming houses and on a large scale in a nearby prison, a 0.5 per cent solution of "gammexane" in CCl_4 gave complete freedom from bedbugs for a period of over six months.

Musca domestica and Culicidae: "Gammexane" reacts surely against the housefly and mosquito by spraying 5 cc. of an alcoholic solution (two per cent) per cubic meter of room. The flies were killed within one hour, and after ten minutes nearly all flies were so paralyzed that they could no longer fly. When sprayed on surfaces in suitable solvents, "gammexane" remained as a nearly invisible deposit and acted as a contact insecticide for several months. Since "gammexane" is stable at high temperatures, we were able to apply it as a vapor by heating on hot plates.

Preliminary tests showed "gammexane" to be five to ten times more effective than any other insecticide to date against many other household insects, such as carpet beetles, clothes moths, fleas, lice, silverfish, and ants. These insects were killed on contact with a residue left by spraying 50 mg. per sq. ft. of surface. Its agricultural and veterinary uses have given highly promising results.

INSECTICIDAL PREPARATIONS

"Gammexane" may be formulated into various preparations similar to dichloro-diphenyl-trichloroethane. A powder form may be prepared by grinding 10 per cent of crude "666" with fine talc. This can be further diluted for use on crops. For some uses the material is mixed in an organic solvent. The solvents used in practice include xylene, carbon tetrachloride, and perchloroethylene. Solutions containing 5 per cent "gammexane" or more may be diluted for use with kerosene or other suitable oil. By the addition of an emulsifying agent concentrated solutions can be prepared which on addition of water give stable emulsions.

Unlike many insecticides "gammexane" has proved to be exceptionally stable to high temperatures. This enables it to be volatilized from hot plates, producing an insecticidal smoke. By these means the insecticide may be used directly against insects or to give a toxic invisible film on surfaces. This method is being studied further.

TOXICITY

Pharmacological investigations conducted by Dr. H. Taylor in England indicate that "gammexane" is relatively nontoxic to animals and man. The effect of absorption through the skin was investigated in our laboratories by painting the bodies of rats with an emulsion containing 10 per cent of the insecticide. No ill effects were observed. "Gammexane" powder was also allowed to come in contact with the laboratory workers' skin for 30 days without any apparent effects.

[4] I am indebted to Mr. Harold I. Stern, without whose help and knowledge the practical tests outlined in this paper could not have been made.

Some Small-Scale Organic Preparations[1]

L. O. BINDER

Montana State College, Bozeman, Montana

INTRODUCTION

FOR a number of years the author has been searching for ways to increase student interest in organic laboratory work. Frequent complaints that "it takes too long" seemed to indicate that the semimicro procedures so successfully advocated by Cheronis[2] and others might offer a partial solution. Preliminary trials with selected students soon showed that in addition to the advantages of simple equipment and less time for preparation, there was also the disadvantage that the students felt considerable disappointment over the small amount of product.

Starting with the idea of obtaining an appreciable yield, a number of procedures have been worked out and several additional pieces of suitable equipment have been added to the list generally used. Since it is felt that the term "semimicro" is not strictly applicable, the expression "small-scale" is suggested in its place. The preparations given are representative of those used in the first two quarters at Montana State College. The list is augmented each year through the assignment of a "problem" to each student in which he is asked to select a particular reaction of interest to him and work out the details of a small-scale procedure. Particular emphasis is placed on solid products since crystallization technique is more difficult to master than distillation.

PROCEDURES

Phenyl urea. Bring a mixture of 1.5 g. (1.5 ml.) of aniline, 2.3 g. of nitrourea, and 20 ml. of water to a boil. Allow to stand for 20 minutes. Cool thoroughly and filter. Re-crystallize the product, using Norite, from 15 to 20 ml. of water. Phenyl urea melts at 147°C. (As an interesting variation, *p*-phenetidine may be substituted in equivalent amount for the aniline. The resulting product, known as "Dulcin," has an intensely sweet taste.)

α-Hydroxyisobutyric acid. Place in an 8-inch tube 6 ml. of water, 3.6 g. (4.6 ml.) of acetone, and 4.0 g. of potassium cyanide. Shake to dissolve as much of the cyanide as possible. Dissolve 6.5 g. of sodium bisulfite in 10 ml. of water. Warm the cyanide solution to about 40°C. and add the bisulfite solution in small portions, stoppering securely and shaking for two or three minutes between additions. When all the bisulfite solution has been added, add an additional 1.5 g. of solid sodium bisulfite, stopper, and shake for ten minutes. Cool the tube in cold water and allow the emulsion to break as completely as possible. Decant the liquid into a separatory funnel without allowing too much of the solid to be carried along. Carefully separate the upper layer and transfer it to an 8-inch tube. Add 1.5 volumes of concentrated hydrochloric acid and warm under reflux with a boiling water bath for three hours.

Fit the tube with a stopper holding a capillary which reaches to the bottom of the tube and a connection to the suction pump, and remove the liquid as completely as possible under vacuum while continuing the heating. To the dry residue add 30 ml. of benzene and arrange for distillation. Be sure to clamp securely as "bumping" may occur. Distill until the benzene comes over water free, then reflux for a few minutes and filter hot. Cool the filtrate thoroughly and filter with suction. This filtrate may be used for a second extraction of the solid residue from the first (hot) filtration. Combine the first and second crops of crystals, recrystallize from benzene if necessary, and dry in air.

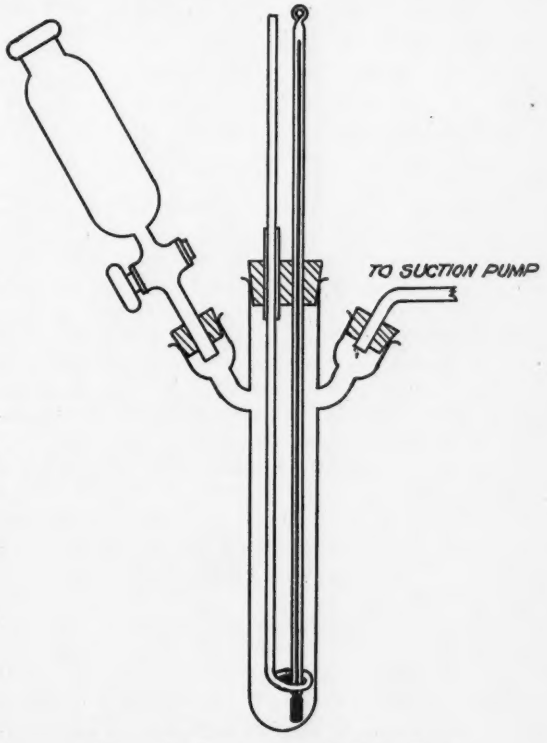


FIGURE 1. PREPARATION OF ADIPIC ACID

[1] Presented before the Division of Chemical Education at the 109th meeting of the American Chemical Society in Atlantic City, April 8–12, 1946.

[2] CHERONIS, N., "Semimicro and Macro Organic Chemistry," Thomas Y. Crowell Company, New York, 1942. Also numerous articles in the JOURNAL OF CHEMICAL EDUCATION.

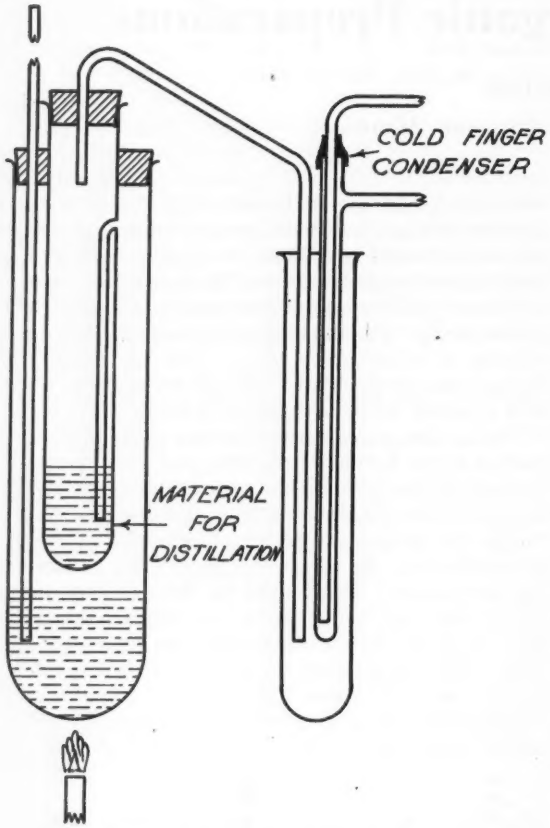


FIGURE 2. STEAM DISTILLATION

Do not leave exposed to the atmosphere for longer than necessary to dry completely. α-Hydroxyisobutyric acid melts at 79°C.

Adipic acid. Fit a three-neck tube[3] with a separatory funnel in one arm and a bent piece of glass tubing connected to the suction pump by rubber tubing in the other. Bore the center cork to hold a bearing of 8 mm. or larger glass tubing and a thermometer. Bend a piece of 6-mm. glass rod into a loop at one end. This loop must fit inside the tube and pass around the thermometer which reaches nearly to the bottom of the tube. The rod should fit very loosely in the glass bearing. (See Figure 1 for diagram of the assembly.) Place 11 ml. of concentrated nitric acid in the tube and 5 g. (5.2 ml.) of cyclohexanol in the separatory funnel. Have ready a beaker of ice water to moderate the reaction if necessary. Turn the suction pump on full and add the cyclohexanol a few drops at a time to the nitric acid.

Stir constantly and rapidly, and watch the temperature closely. Add the cyclohexanol at such a rate that the temperature stays between 85° and 90°C. The addition should take about 15 minutes. When all the cyclohexanol has been added, maintain the temperature at 80–90°C. for 15 minutes with a small burner; then cool the reaction mixture in an ice bath and filter the product. Wash with about 10 ml. of ice water and allow to dry. Adipic acid melts at 151–3°C.

o- and p-Nitrophenol. Dissolve 9.6 g. of sodium nitrate in 24 ml. of water in an Erlenmeyer flask. Carefully add 6.5 ml. of concentrated sulfuric acid. Cool to 20°C. and add drop by drop 6 g. of phenol which has been liquefied by warming with 1 ml. of water. Keep the temperature between 20° and 25°C. during the addition of the phenol. Let stand for an hour or more with shaking, then add 2 volumes of water. Decant the aqueous layer carefully and wash the residue thoroughly with water twice, decanting the water each time. Steam distill the residue. (See Figure 2.) The *o*-nitrophenol that passes over is allowed to crystallize and then filtered with suction and dried. It should melt around 45°C. Impure material can be re-distilled with steam.

The residue in the original steam distillation tube contains *p*-nitrophenol which is not volatile with steam. To recover this material, add 2 *N* sodium hydroxide until the solution is just alkaline to Congo paper, then add an additional 12 ml. of 2 *N* sodium hydroxide. Add 0.5 g. of Norite and pass steam through as in steam distillation for five to ten minutes. Filter the hot solution and concentrate to 10 or 15 ml. On cooling, this solution should deposit crystals of the sodium salt. (If no crystals appear, rewarm this solution, add 3 or 4 ml. of 1 *N* sodium hydroxide, and allow to cool again.) Filter the precipitate with suction and wash it with a little 2 *N* sodium hydroxide. Liberate the free *p*-nitrophenol from the salt by adding dilute hydrochloric acid dropwise to a hot water solution of the salt. The product appears as an oil that crystallizes on standing. Recrystallize using Norite or Darco from very dilute hydrochloric acid. *p*-Nitrophenol melts at 114°C.

n-Propyl acetate. In an 8-inch test tube reflux 5.2 g. (5 ml.) of glacial acetic acid, 4.8 g. (6 ml.) of *n*-propyl alcohol, and 7 to 8 drops of concentrated sulfuric acid for 45 minutes. Arrange for distillation and distill until the temperature reaches 110°C. Treat the distillate with 3 or 4 ml. of saturated sodium carbonate solution or until you get a basic reaction to phenolphthalein. Transfer to a separatory funnel, withdraw, and discard the lower layer. Wash the crude ester with 3 or 4 ml. of water, withdraw, and discard the water, then add five or six granules of anhydrous calcium chloride and allow to stand with shaking for five or ten minutes. Decant into a dry test tube, add more calcium chloride, and allow to dry for an additional 10 or 15 minutes. Filter into a small distilling tube and distill. *n*-Propyl acetate boils at 101.6°C. (760 mm.).

Cyclohexanone. Dissolve 8 g. of sodium dichromate in 20 ml. of water; add 4 ml. of concentrated sulfuric acid. Place in a 10-inch pyrex test tube 5 g. (5.2 ml.) of cyclohexanol and add the dichromate-sulfuric acid

[3] The three-neck tubes have been fabricated by the author, but should be readily obtainable at moderate cost from Corning, Ace Glass, Scientific Glass Apparatus Company, etc.

mixture in small portions, cooling under the tap to 20–25°C. between additions. Use a thermometer as a stirring rod and do not allow the temperature to rise over 50°C. When all of the dichromate-sulfuric acid mixture has been added and the temperature no longer tends to rise above 50°C., place the tube in a beaker of water at 50–55°C. for 15 to 20 minutes.

Add 20 ml. of water and arrange for distillation. Distill until the solution commences to foam. Separate the cyclohexanone layer in the receiver carefully and extract the water layer with 10 ml. of ether. Combine the ether extract with the cyclohexanone, dry with a small amount of anhydrous calcium chloride, and transfer to a distilling tube. Remove the ether with a water bath and distill the product. Cyclohexanone boils at 156.7°C. (760 mm.).

Class reaction has been very satisfactory, particularly where students have had an opportunity to compare macro and small-scale procedures. The fact that a respectable yield is possible is important from the student's point of view. The knowledge that careful work will produce results encourages him to acquire good technique and to be willing to repeat a preparation if the yield is low. No preparation was assigned for which the author was not able to get a 60 per cent yield, and in most cases the class average yield is 50 per cent or better.

As given at Montana State College, the laboratory work is supplemented with in-the-laboratory lectures and demonstrations on distillation, boiling points, crystallization, and melting points, calculation of theoretical yields, and other pertinent matters of theory and technique. During the first quarter an excessive amount of supervision is not necessary, and during the second, very little except for checking equipment setups.

The Precious Sweep Stakes

A $10,000 bracelet adorning the wrist of a Hollywood movie star may contain some gold which was part of the bridgework of a Phoenician who lived 2500 years ago. Or perhaps it may contain gold mined in Egypt more than 3200 years ago during the reign of Rameses II. Ancient Asiatic silver may be part of the glittering knives, forks, and spoons which grace the dinner table of His Majesty King George VI of England. And the platinum necklace and wedding ring of a Park Avenue bride may contain metal from some old Russian rubles. Gold and platinum live through the ages. They are precious metals which have been used over and over again with little loss in volume. Silver, too, has through many centuries been recovered from old articles to be used again to make new ones, perhaps totally different in form.

In the United States today there are few plants engaged in recovering precious metals and others of value from such prosaic sources as jewelry manufacturers' floor sweepings. One of these plants is the Irvington Smelting & Refining Works, Irvington, New Jersey. In addition to gold, silver, and platinum the Irvington plant also recovers such valuable metals as palladium, osmium, iridium, and rhodium, which are usually found associated with the gold or platinum.

Floor sweepings, however, are not the only source of the company's precious metals. The plant receives shavings, dust, and other metal particles which are collected in receptacles on metal cutting machines in jewelry plants.

A carload of gold or platinum false teeth and tooth fillings containing gold, silver, or platinum may find its way to the Irvington plant. The plant also recovers silver from used photograph developing solutions and other chemicals, and gold from bottles which contained artists' gold paint and to which some paint still adheres. Chinaware with gold or platinum decorations and used chemicals containing these metals are other sources of supply. The Irvington plant may purchase copper (called copper bullion) from some smelters of the red metal because it contains gold or silver. Irvington may process in its plant the copper that remains after refining, or it may sell the copper. Irvington may buy matte—copper sulfides containing gold or silver—or it may purchase copper concentrates (partly refined copper ore) because they contain gold or silver.

Hundreds of tons of metal-bearing materials must be smelted and refined every day by Irvington to produce sizable amounts of precious metals. Largest production by weight is in silver, which may run as high as 3,000,000 ounces per month, sold at the established government price of 71 cents per troy ounce. Production of other precious metals is relatively small, prices high ....

The reason palladium, osmium, iridium, and rhodium can be recovered is because these are generally associated with platinum and, in fact, are called the platinum metals. They impart certain desirable properties to platinum. Palladium, which resembles the light gray platinum in color, is usually found in platinum ore. It imparts hardness to platinum, but it also is used in some grades of so-called white gold, as a metal plating, or, in the form of leaf, as an ornamental coating for base metals, or even wood. Palladium is used as an alloy in dental gold.

Osmium, also light gray in color, gives extreme hardness to platinum, but its biggest application is as an alloying agent for fountain-pen tips. It is alloyed with iridium, the grayish white metal with which it is generally found in nature. Iridium alone, however, also is used as a hardener for platinum.

Rhodium is, perhaps, the rarest of platinum metals. It often is used as a pinkish plating for jewelry, but because of its high melting point, 3542°F., it finds more valuable applications in thermocouples, in chemical apparatus exposed to high temperatures or to certain acids, and in electric furnaces where it is used as resistance wire. Its high reflectivity also makes rhodium valuable as a coating for searchlight reflectors.

With the exception of silver, these precious metals seem to possess permanent useful lives exemplified by the characteristics of gold and platinum. Gold, with its hundreds of applications, is used largely because it resists the action of practically all acids and alkalies. It is, however, soluble in aqua regia, a mixture of nitric and hydrochloric acids. Gold is the most malleable of all metals and for this reason, and the fact that it will not tarnish, it is used in the form of leaf. One gram of gold can be beaten into leaf only 0.0000033 inch thick which covers an area of six square feet. One gram can be drawn into 1.5 miles of wire.

Platinum is harder than gold, but like this metal it is generally alloyed with other metals to produce the desired hardness. Platinum-iridium alloy, for instance, is very hard. It is resistant to corrosion and the action of most chemicals. It is used in instruments, as electrical contact points in magnetos, and for other applications. Platinum has the unique advantage of having electrical resistance that varies directly with temperature. For this reason it is used in apparatus which can measure temperatures very close to absolute zero.

The Irvington Smelting and Refining Works is associated with other companies which form Engelhard Industries. This organization was established and is owned by Charles Engelhard, widely known in the field of precious metal refining.

Mr. Engelhard first became interested in establishing platinum metal refining in this country around 1900 when he realized

that the business was almost entirely in the hands of foreign refiners, some of which he represented here. Mr. Engelhard's first move toward establishing an industry here was made in 1902 when he purchased the American Platinum Works at Newark, New Jersey. The plant refined jewelers' filings and sweepings, assayed bullion, delivered platinum sheet and wire, and made platinum utensils for the chemical industry. It also produced platinum alloys for the dental profession and other alloys for use as electrical contacts, such as those used for magneto breaker points. The company also developed automatic machines for applying iridium tips to gold and stainless steel pens. The platinum refining end of this business is continued today.

In 1904, when Baker & Company, Newark, was incorporated, Mr. Engelhard became general manager and treasurer and later acquired the company. It refines platinum metals, gold, and silver, and produces such products as platinum-rhodium, which is used as a chemical catalyst. It develops rhodium plating for jewelry manufacturers and supplies such manufacturers with findings, settings, ring blanks, and other precious metal products. It makes platinum spinnerets for rayon manufacturers and platinum alloys for use in thermostats.

In 1905 Charles Engelhard established the Hanovia Chemical Company at Newark to manufacture precious metal paints for use on chinaware, scientific apparatus made of pure fused quartz, and a line of therapeutic lamps such as those which produce ultraviolet and infrared light. It also makes platinum resistances for laboratory electric furnaces.

After Mr. Engelhard purchased the Glorieux Smelting & Refining Works at Irvington in 1907, he changed the name to Irvington Smelting & Refining Works. Later Mr. Engelhard also acquired or established a number of other companies including some in Japan, England, and Canada.

Irvington's affiliates sometimes have available certain materials containing precious metals but which are shipped to Irvington, because it is best able to do the refining.

The Irvington business is unique in at least one respect. It deals with raw materials of unknown value at the time they are received. It accepts materials for refining before it knows what to pay and before the seller knows how much to charge for it. Every shipment, therefore, must be assayed, and the seller usually has an agent on hand to see the results of the assay. In the case of bullions and other metals, sample drillings are analyzed to determine the quantity of precious metals in them. If the metal comes in the form of small pieces, they are melted and cast into bars so that drillings can be obtained.

It is not so easy to place a value on sweepings. Each shipment of sweepings is ground to powder fineness in a mill and then it is well mixed. If the shipment is contained in many barrels or drums, the contents of each container is sampled, and the samples are mixed to obtain an average of the entire shipment. The powder is dumped on the floor and divided into quarters Samples are taken from each quarter and analyzed for precious-metal content. Average precious-metal content of the four analyses is the basis for evaluating the shipment. The market price of the precious metals minus the refining charge is then paid to the seller.

All materials are not processed in exactly the same way. Copper bullions, high-grade sweepings, concentrates, and similar materials of high metallic content, for instance, are not usually smelted in a blast furnace but go directly to cupels, or small squat reverberatory furnaces. Low-grade sweepings and other materials are smelted in a blast furnace together with lead because lead picks up or acts as a carrier for gold, silver, and platinum.

A typical blast furnace charge may consist of sweepings mixed with water, pig lead, or lead matte recovered from a previous charge, coke, litharge, and fluxes such as limestone and gypsum. When the furnace is tapped, the slag is poured from one side and the lead with its precious metal content, called lead bullion, from another side of the furnace. The lead bullion which is high in silver content is poured into iron pots.

If there is any lead matte in the mass, it will rise to the top of the pot where it solidifies and is removed. The bullion is cast into pigs. Matte and bullion are processed as described later to effect a parting, or separation, of precious metal from base metal.

In some cases a blast furnace is charged without lead as, for instance, when the material produces matte merely by being smelted. The composition of some materials, such as copper concentrates, permits the addition of low-grade sweepings which increase the copper matte yield. This also makes it unnecessary to smelt the sweepings with lead.

When copper matte is produced, it is reheated in a forehearth and then is treated in a converter, or rotary furnace. Air is blown through the converter to oxidize the sulfur in the concentrate.

Lead matte also is treated in a converter, but only after it has been used repeatedly. The converter produces copper bullion and slag. The copper bullion is poured into cold water which causes it to be formed into shot. The slag consists essentially of iron and lead usually contained in the matte. It is used as blast furnace flux.

The copper shot is charged into lead-lined tanks in which it is treated with sulfuric acid solution through which steam and air are forced. The result is the formation of copper sulfate and a slime. The slime contains the precious metals. The copper sulfate is crystallized and sold. The slime is roasted, leached with sulfuric acid in lead-lined agitators to remove any copper, and then it is filtered. The slime is charged into an oil-fired cupel furnace together with lead bullion made in the blast furnaces. The cupel furnace also may be charged with high-grade bullions and concentrates that are purchased by the company.

When lead bullion is melted in the cupels, the result is silver bullion and molten litharge. The litharge floats upon the molten lead and is allowed to overflow into pots. This litharge, lean in precious metals, is returned to a blast furnace. The silver bullion in the furnace hearth, comparatively free of lead but carrying gold and the platinum metals, is poured and cast into anodes or slabs.

If the silver bullion is low in gold and platinum metals, it is cast into anodes, which are sent to the electrolytic silver department. If, however, there is a large quantity of gold and platinum metals in the bullion, it is cast into thin slabs to be used in the parting process to expedite the recovery of the gold.

In the parting plant silver bullion, called Doré silver, is treated with boiling sulfuric acid in iron kettles heated by oil burners. The resulting silver sulfate solution is decanted off from the slimy residue, which consists of gold and the platinum metals. The residue is refined electrolytically to part the gold and platinum metals.

Silver is removed from the sulfate solution by passing it over copper sheets. The silver deposits on the copper sheets. The copper sheets eventually dissolve to form copper sulfate. The silver in the form of fine particles is melted, cast into anodes, and used in an electrolytic cell. This further refining of silver by electrolysis is necessary to remove platinum metals present. Silver nitrate is used as electrolyte, and the silver anodes are wrapped in muslin sacks which pick up slimes which contain gold and platinum metals.

Mechanically operated glass rakes break off the long silver crystals as they form upon the silver cathode. The crystals fall to the bottom of the cell and at regular intervals are removed. The silver crystals taken from the cell are washed, dried in a centrifuge and, after being melted in crucibles, are cast into bars and then shipped.

The slimes left in the muslin sacks contain gold and other precious metals and are refined in the same manner as residue from Doré silver treatment.

Residues from the parting process and slimes from the silver refining process are melted and cast into anodes, which are used in electrolytic cells in which the electrolyte is gold chloride solution containing some free hydrochloric acid. Gold is deposited on the cathode and is scraped off, melted, and cast into bars and shipped.

The slimes from the gold electrolysis, which consist largely of silver, gold, and platinum metals, are chemically treated to separate the various metals.—Reprinted from *Esso Oilways* (March, 1946)

Colloidal Metals in Nonaqueous Solvents

by the Bredig Method

ROBERT C. CROSSON, JR.
HAROLD J. ABRAHAMS

Central High School, Philadelphia, Pennsylvania

THIS paper presents the results of experiments with the preparation of metallic colloids in nonaqueous media by the Bredig method. Two classes of methods are in use for the preparation of colloidal dispersions, coagulation or condensation and peptization or dispersion. In each method the aim is to produce a condition in which the particles of the dispersed substance are in a state of very fine subdivision. These methods may be summarized as follows:

Coagulation (condensation): This method is exemplified when a few drops of ferric chloride are added to boiling distilled water. The ferric hydroxide molecules produced by hydrolysis coagulate and build up into colloidal particles.

This is a chemical method and is widely applicable in obtaining colloidal dispersions of insoluble compounds which form as a result of (*a*) reduction (gold), (*b*) oxidation (sulfur of H_2S by SO_2), or (*c*) metathesis (insoluble chlorides, sulfates, phosphates, etc., hydroxides by hydrolysis, and sulfides by the use of hydrogen sulfide).

Peptization (dispersion): This method is subject to some variation, but in each variation the aim is the same—that is, to start with larger particles and tear them down to such smallness that they will remain dispersed and not sink.

(*a*) One method of reducing the size of particles until they are capable of passing into the colloidal state is to use a "colloid mill." In this method the material to be dispersed into the colloidal state is merely ground with a liquid between two metal discs which rotate at high speed in opposite directions, until the correct state has been attained.

(*b*) Another method for reducing particle size is to subdivide drops (for example, an oil) into extremely fine droplets (by shaking with water) and then to prevent the droplets from running together again into a pool by coating them with another substance. An example is mayonnaise, in which case olive oil droplets are suspended in vinegar and water, egg being used to coat the oil droplets and thus prevent their coalescing.

These methods of preparing colloidal dispersions provide methods which vary in applicability. Colloids of gold in a wide color range may be easily produced by the addition of certain reducing agents to solutions of gold chloride. Some of these gold colloids are stable for years but require care in their preparation. The use of a colloid mill is, of course, a commercial method. The arc method, on the other hand, is rapid and simple and requires little skill or care, although the product is apt to have a brief existence.

A method for preparing a colloidal dispersion of metals by the use of the electric current was discovered by Bredig in 1897. In this method the metal is first vaporized (from the cathode) by the heat of the arc produced and then condensed. If a trace of potassium hydroxide is added to the water, the dispersed metal is stabilized. This method is a combination of dispersion and condensation. The procedure is:

Two bars of the same metal are attached to a source of electric current and serve as electrodes. These electrodes are immersed in water and brought into contact with each other for an instant to produce an arc, and then separated about 2 mm. A rattling noise generally results, and a colored discharge appears, showing that some of the metal has been vaporized. These metal particles are immediately chilled by the surrounding water and do not therefore have time to assume an arrangement in which they would be too large and dense to be capable of remaining suspended. Thus the electric arc produces a colloidal dispersion of the metal by subdividing it.

Bredig employed currents ranging from 5 to 10 amperes at 30 to 110 volts. He found that a gold dispersion thus prepared contained about 14 mg. of the metal per 100 ml.

We have prepared the following colloids in nonaqueous dispersion using the Bredig method and a coil from an ordinary household toaster (610 watt, 110 volt) attached to a 115 volt a.-c. source.

Dispersing medium	*Dispersed metal*
Glycerin	Hg, Al, Sn, Fe, C
Methyl alchol	Hg, Fe Zn
Mineral oil	Hg, Al, Fe, Zn, C
Turpentine	Ca Zn
Benzene	Ca, Zn
Formaldehyde	Hg, Fe, Zn

Bars of the metal were attached to wires from the 110-v. a.-c. circuit with the coil of a household toaster in series, and an arc struck as described above.

In the case of mercury the wires ended in a pair of carbon electrodes which were dipped into two little pools of mercury, and the pools made to approach each other closely enough to produce an arc.

All of the colloids mentioned were found to yield a Tyndall cone.[1] They remained stable in varying degrees for at least three months, the supernatent liquid still producing the Tyndall cone even after settling had taken place. Most of these colloidal dispersions were gray in color, except those of tin and iron which were brown.

[1] For a description of the apparatus used for this purpose, see H. J. ABRAHAMS AND A. DUBNER, JOURNAL OF CHEMICAL EDUCATION, **20**, 61–2 (1943).

Out of the Editor's Basket

IF YOU (like myself) never knew what Guar is, you will be interested in a little pamphlet issued by General Mills (Minneapolis, Minnesota), "The Story of Guar." It is a drought-resistant, pod-bearing legume first introduced into this country in 1903 but important only for the last five years, the war having brought out some of its characteristics. It seems that it contains a certain polysaccharide, a mannogalactan, of unusual and useful character.

The chief constituent of guar flour, responsible for its colloidal properties, is a polysaccharide resembling starch in chemical structure except that on hydrolysis the two hexose sugars, mannose and galactose, are obtained instead of dextrose.

This mannogalactan is dispersible in either cold or hot water, producing colloidal dispersions of exceptionally high viscosity at low concentrations. The sols thus produced do not set to a gel but remain in thick sol form. When such a sol is dried, a transparent film is produced which is much more flexible than a starch film. Guar flour has four to eight times the thickening power of starch.

Guar flour exhibits properties both of stabilizers and coagulants. It may be used to stabilize suspensions or emulsions; or, by varying conditions and concentrations, a separation of the dispersed phase may be accomplished without coagulation. In paper pulp, flocculation of the fibers is retarded, while in bentonite suspensions, flocculation can be accelerated.

Among other general characteristics of guar flour these points may be of interest. The addition of borax solution to a sol will cause formation of a thick gel. If tannin is added to a sol, a separation of a gum-tannin complex takes place. This may be redispersed by heating but will again be precipitated on cooling. Aqueous dispersions are practically neutral in reaction. Dilute acids, alkalies, and electrolytes cause relatively little change in viscosity. Strong acids will cause hydrolysis and loss of viscosity. Alkalies tend to cause darkening and also cause some decrease in viscosity. The mannogalactan is precipitated out of the aqueous sols of guar flour by alcohols, acetone, etc.

Antifoam

Foaming is frequently a very serious problem in chemical processes and industrial operations. Aqueous alkaline solutions in particular are subject to such severe foaming that sometimes processing becomes extremely difficult. Industrial operations that are frequently complicated by excessive foaming include steam distillation and vacuum evaporation. Dow Corning now offers an entirely new silicone compound developed especially for use against foam in aqueous solutions and emulsions.

Quartz Crystals

Some German methods for growing quartz crystals appear to have advantages over American methods.

One method involved use of alkali halide crystals, derived from specially purified salts, as prisms in the ultraviolet monochromators. Use of pure salts reduced the crystals' sensitivity to water vapor. The prisms were always mounted on slightly heated tables to prevent fogging. Crystallization occurred from the top of the molten salt downward.

To start the process, a small piece of salt was mounted in a water-cooled holder and lowered until it touched the top surface of the molten salt contained in a porcelain crucible. The water cooling caused the crystal to grow. As it became larger, the crystal was raised slightly to permit continuing growth. Finally, the crystal was removed and placed in an annealing oven at 500°C. for 24 hours, after which it was cooled for four or five days. Crystals produced in this way are said to be as homogeneous as good optical glass.

Acetylene

Advanced acetylene chemistry was one of Germany's answers to her acute shortage of petroleum. German research led to production of a wide range of new products including plastics, adhesives, thickening agents for cable and leather oils, leather impregnates and protective coatings, textile finishing and sizing agents, solvents, explosives, and raw materials for lacquers. In the field of medicine, polyvinyl pyrrolidone, one of the products developed through acetylene chemistry and known commercially as "Periston," is used in blood transfusions and to prevent bleeding.

Experiments with acetylene resulted in the discovery of a great number of fundamentally new reactions for this gas. One of the surprising things was that aromatic hydroxy compounds can react with acetylene under the influence of certain catalysts in such a manner that resinous polymers can be obtained directly through intermediately formed hydroxystyrenes.

Fundamentally new reactions resulting from the use of copper and silver or their compounds, especially their acetylides, as catalysts were also observed. These observations opened up the chemistry and the industrial utilization of the ethynyl compounds. The use of nickel catalysts led to a completely new polymerization reaction yielding cyclic polyolefins.

Suntan, Etc.

A 10-page booklet describing sunscreening agents, with charts of various tanning and sunburning rays and formulas which meet the requirements of suitable suntan preparations, has been issued. Instructions for preparing the formulas are included. Copies of the booklet are available upon request to Givaudan-Delawanna, Inc., 330 West 42nd Street, New York.

Microwave Tubes

Tiny electron tubes operating at very high frequencies may revolutionize inspection and control of hundreds of industrial and agricultural products and assure better quality products for the home. According to M. A. Acheson of Sylvania Electric Products, Inc., the developers of the new tubes, the microwave system might be arranged to accommodate the passage of

many mass-produced products directly through the microwave circuit to indicate faults of structure, composition, degree of moisture content, impurities, surface hardness of metals, ripeness of fruits, and many other characteristics now requiring expensive laboratory testing and frequently involving the destruction of a percentage of production.

The kind of product that may be explored is almost without limit. Crankcase oil might be quickly tested to determine whether or not it needs to be replaced. The microwave system could indicate worms in fruits and vegetables, the amount of solvent in paint, the depth of surface hardness of ball bearings, the moisture in lumber, and structural flaws in pipe, molded plastics, and other composition articles.

Veterans' Colleges

"It's time for colleges to get off their campuses," was Washington's comment as interest in veterans' education rose to new heights. General Bradley, Veterans' Administrator, offered similar advice: "If Columbia, Stanford, Brown, and other colleges would set up annexes, even if these annexes were miles from the campus, (veterans) would have the benefit of the traditions of the college."

General Bradley's top assistants, meanwhile, had concluded a survey of college vacancies for veterans and decided that the situation is "very encouraging."

"A veteran can get into a school if he is willing to go where vacancies exist," said Brigadier General H. B. Lewis and Nelson R. Hensen of the VA. The institutions in which vacancies exist and in which vacancies "are apparent" are now being listed in a guide to be issued in a few days.

Photo Reproduction

An inexpensive photo reproduction process developed at Focke-Wulf, Bad Eilsen, Germany, which may replace the normal drawing-board method for production drawings, particularly in small business concerns, has been reported by an American technical investigator. Many of the advantages of the process, it is admitted, are equaled if not surpassed by American methods. Installation of the Focke-Wulf process, however, is less expensive.

The drawing board used in this process consists of a sheet of frosted glass mounted in a wooden frame and set in a horizontal plane. The drawings are made in pencil on the surface of frosted glass and then gone over with a special waterproof ink. Erasures may be made by means of steel-impregnated pencils of varying degrees of hardness.

A transparent sheet of cellulose material known as "Astrolon" is then coated on one side with an emulsion which has a potato meal base. The sheet is dried and then weighted down to the drawing to insure full surface contact. It is subjected to four or five minutes' light treatment from lamps below the drawing table. The prepared surface is brushed over with a solution of glycerin and mill acid, which acts as a developer, and then rubbed with ink, which sets the lines by chemical action. The surface ink is removed in a water bath. The frosted glass may be cleaned with ink eradicator and re-used. This "Astrolon" negative is the master drawing from which innumerable copies may be made.

Four basic advantages of the process listed by the investigator are: (1) economy of installation brings the facilities of photo reproduction within the reach of small business concerns, (2) repeated use of the same glass drawing surface eliminates continued purchase of sensitized glass, (3) expenditure for reducing and enlarging processes is eliminated, and (4) changes may be made in the drawing both on the glass and on the "Astrolon," which is not possible on the average silver emulsion print or acetate base.

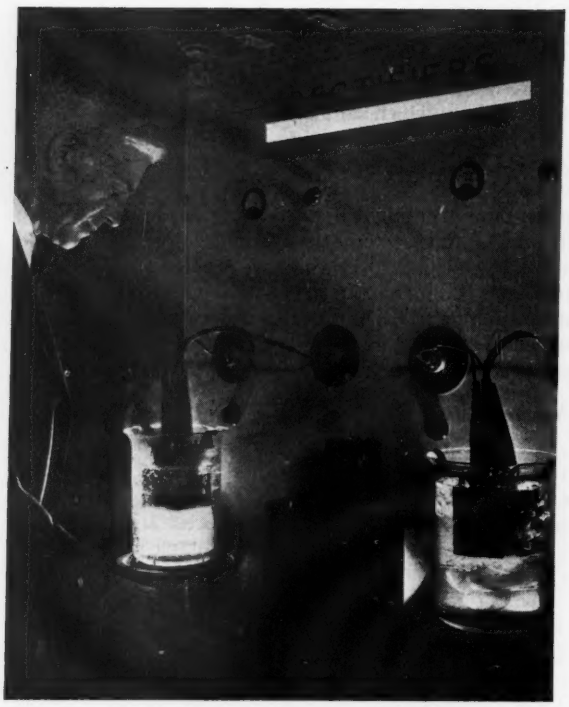
Aluminum

Details of a German carbothermic process for extracting aluminum from clay and results of American experiments in extracting alumina from clay and similar materials by a hydrochloric acid process and by hydrogen chloride gas have been made available to the American public.

The principle of the German process, as described by Dr. Wilhelm Patterson, Director of the Leipziger-Leichtmetall-Werk near Leipzig, is the reduction of alumina at high temperatures in a centrifugal furnace using carbon in the form of coal dust as the reducing agent. The furnace revolves fast enough to keep the molten bath against the sides by centrifugal force. This protects the refractories from the intense heat of an oxygen-reinforced powdered coal flame. An excess of dry coal dust is added as a reducing agent.

The ends of the furnace shell are double and are water cooled to protect the ends of the furnace and the end brickwork from the high temperatures. A variable speed drive is provided to bring the furnace slowly up to speed and to vary the operating speed for optimum performance. The pilot furnace is about 80 centimeters in diameter and two meters long. It can rotate at 350 revolutions per minute.

The American experiments on extraction of alumina were conducted by the Anaconda Copper Mining Company in cooperation with the War Metallurgy Committee of the National Research Council. The hydrochloric acid process consists of calcining clay at about 600°C. to break up the aluminum silicate and render the alumina soluble in acid. The calcined clay is then treated with hydrochloric acid to dissolve approximately 90 per cent of the alumina. The strong solution of aluminum chloride thus formed is separated from the residue by filtration and is evaporated in the usual type of vacuum evaporators equipped with Karbate tubes. The aluminum chloride crystals are dried and calcined at a temperature of 500–600°C. to decompose them into aluminum oxide and hydrochloric acid, the latter being collected in absorption towers for re-use. The crude alumina thus produced is about 90 per cent pure and may be readily purified by the Bayer process.



SELENIUM RECTIFIER IMPERVIOUS TO HEAT, COLD, DAMPNESS. STEAM CAN BE SEEN RISING FROM THE WATER BOILING IN THE BEAKER AT THE LEFT. IN THE OTHER, PIECES OF ICE CAN BE SEEN FLOATING. YET THE TWO HERMETICALLY SEALED SELENIUM RECTIFIERS IMMERSED IN THESE BEAKERS ARE TURNING ALTERNATING CURRENT INTO DIRECT CURRENT AT AN EFFICIENCY EQUAL TO THAT ATTAINED UNDER NORMAL CONDITIONS. SUCH INVULNERABILITY TO HEAT AND COLD CLIMAXES SEVEN YEARS OF RESEARCH BY ENGINEERS OF THE WESTINGHOUSE ELECTRIC CORPORATION.

Rectifier

A newly developed selenium rectifier can be submerged in boiling water or packed in ice and still turn alternating current into direct current at an efficiency equal to that obtained under normal operating conditions, a performance never before achieved with a plate-type rectifier.

The new rectifier, a product of seven years of secret research and development by engineers of the Westinghouse Electric Corporation, consists of a heavily tin plated, hermetically sealed container inside which is placed selenium suspended in oil. It was designed to keep pace with the exigencies of war. It has unequaled invulnerability to high and low temperatures, a quality which insures top performance in any climate from the North Pole to the Equator.

Many unfortunate experiences on battlefronts occurred when the ordinary converting device failed to operate while exposed to heat which mounted as high as 150°F., or to cold far below zero. Motors, relays, signal lamps, controls, and, most important of all, radio and radar quit working. Frequently the rectifiers were ruined and had to be replaced.

An example of a common hazard to rectifier performance is that of a bomber which may stand for hours under the burning tropical sun, then takes off, and a half hour later is flying through the sub-zero temperatures of the stratosphere. The usual rectifier decreases markedly in efficiency as either heat or cold intensifies beyond a certain range and breaks down completely when the surrounding temperature gets to about 150°F. or to 40° below zero F. The plane is then left without communications and other accessories which depend upon direct current from converters. This new selenium rectifier will keep right on working under the most extreme conditions of temperature.

Industrial electrical control devices, transformers, resistors, vacuum tubes, rectifiers, and other heat-dissipating apparatus are usually mounted inside a metal cabinet, resulting in extremely high temperatures that mitigate against good efficiencies and long life for ordinary rectifiers. This new selenium rectifier will operate with only a slight drop in current output at a total temperature higher than the boiling point of water and will last much in excess of 1000 hours.

Extremes in temperature are not the only enemies of the rectifier. By actual test, salt spray does not interfere with the performance of the new selenium rectifier, but it will destroy an unprotected rectifier on the deck of a ship in a few hours. In tropical areas insects, fungi, and humidity quickly ruin the ordinary open-type rectifier, but the hermetically sealed selenium unit is impervious to their attack.

Colored Cotton

Research and experimentation conducted over a long period by Soviet Russia in the development of colored cottons in the field have been reported. According to reports from the U.S.S.R., where experimentation has given way to actuality, rose, lemon, brown, and green cottons were being grown on an area of 3700 acres in 1945. The yield was expected to be over 700 tons, or a million yards of naturally colored cloth.

The new material was to be used in the manufacture of counterpanes, knitted fabric, diagonal cloth, and decorative cloths. Some 500 samples of fabrics have been manufactured from this cotton—the browns of which went into uniforms.

Color fastness of the fabrics, according to Russian sources, is greater than that of fabrics made from cotton colored with artificial dyes. American cottons with green or brown lints have been known for some time, but are not grown on a large scale.

Slide Rules

Transparent Plexiglas is now used for making minutely calibrated slide rules which defy temperature changes, humidity, and all factors that formerly affected old-fashioned wooden devices. Application of Plexiglas—the same material that provided bomber noses during the war—to the manufacture of drafting instruments marks another step in the reconversion of this acrylic plastic.

Eye Pigments

Rats and humans have this in common with salt-water fishes—that the rods of the retinas of their eyes contain the same kind of pigment. This pigment, which allows them to see in a dim light, contains vitamin A. Deprived of vitamin A, people become night blind. Fresh-water fishes have a different kind of visual pigment formed from recently recognized vitamin A_2.

During some discussions in 1942 by the War Research Committee of the Rochester Chamber of Commerce, it was decided to try to change the "salt-water" pigment of rats—and perhaps humans—to the fresh-water type on the long-shot gamble that it might improve the ability to see in a dim light. To do this it was necessary to deplete the subjects of ordinary vitamin A and feed them large quantities of vitamin A_2. This posed a tremendous problem because vitamin A_2 was nothing but a chemical curiosity; however, Dr. N. Embree, with members of the War Research Committee of the Rochester Chamber of Commerce, collected livers from walleyed pike and various fresh-water fish from all over the United States. The liver oil was extracted and molecularly distilled to give enough vitamin A_2 for the experiment.

The laboratory rats were depleted under the direction of Associate Professor Harold Hodge and his assistant, Mr. J. H. Wills, Jr., both of the University of Rochester School of Medicine and Dentistry. The rhodopsin of the rats was gradually displaced by the fresh-water porphyropsin. These were probably the first rats in history to see things in the same manner as a brook trout! The experiment was repeated with human volunteers, but results have not been announced.

Fellowships

The establishment of 22 graduate fellowships at 17 educational institutions by Standard Oil Company (Indiana) was announced by Dr. Robert E. Wilson, chairman of the board, who said the purpose of the program is "to provide 'seed corn' for future research."

Fellowships in chemistry have been established at Northwestern, Illinois, Chicago, Wayne, Ohio State, Wisconsin, Iowa State, and Johns Hopkins; in chemical engineering at Massachusetts Institute of Technology, Minnesota, Illinois, Cornell, Carnegie Tech, and Princeton; in engineering at Michigan, Minnesota, Iowa, Illinois, Purdue, and Illinois Institute of Technology; in civil engineering at Purdue; and in marketing and management at Northwestern.

The fellowships will be awarded to students working for masters' or doctors' degrees. They will vary somewhat in amount, depending on the tuition and other fees at the various institutions, but the average for each fellowship will be approximately $1500 a year. The work done will be basic research, and the results will be published in accordance with the usual academic practice. Holders of fellowships will be under no obligation to Standard Oil as regards subsequent employment. The sponsoring company will also receive no rights to any patents resulting from the work.

New Award to Educators

This year for the first time a new award of $1000 will be given to the college or university teacher adjudged to have contributed most to the successful teaching of engineering students. The prize, to be conferred annually, will be known as the George Westinghouse Award in Engineering Education. Established to commemorate the 100th anniversary of the birth of the famed inventor, the award has been made possible by the Westinghouse Educational Foundation.

In announcing the plan, Dr. Harry S. Rogers, President of the Society for the Promotion of Engineering Education and President of the Polytechnic Institute of Brooklyn, made clear that while there are no age limitations in making the award, "consideration will be given especially to the younger men who show by their past records evidence of continuing activity as superior teachers." He continued, "The George Westinghouse Award has single significance as the first of its kind to be presented in recognition of distinguished teaching of engineering students."

The Society for the Promotion of Engineering Education is the national organization of engineering teachers and educators, and numbers among its members most of the established professional teachers of engineering in the United States. The George Westinghouse Award is one of several medals and awards annually granted by the Society.

Cotton Picking

Science marches on! This time it has opened the doors to successful operation of mechanical cotton picking at six cents to seven cents per pound. Chemical defoliation is the new hand-labor saving method. Calcium cyanamide, when dusted and settled on the leaves of the cotton plant, dissolves in the dew. This solution interferes with respiration. And bingo, within a few days the leaves break off. Thus, defoliation permits the mechanical picker to operate at maximum efficiency with no leaves to interfere with its action.

Why Not?

Some time ago a great soldier, General Dwight Eisenhower, received an honorary degree. In the course of his formal remarks on that occasion, the General turned to President Marsh of Boston University and said, "Why doesn't the educational world put my profession out of a job?"

Radiation Detection

Wartime developments for the detection of radiation in the thermal region were released recently by the National Defense Research Committee.

Outstanding developments were on bolometers, of which two distinctly new types were produced. One bolometer, made of thermistor materials, was developed at the Bell Telephone Laboratories by Dr. J. A. Becker and his associates. Consisting of thin flakes of mixtures of nickel, manganese, and cobalt oxides (semiconductors) ranging in size from 0.1 to 1.0 millimeter wide, 1.0

to 5.0 millimeters long, and 0.01 to 0.02 millimeter thick, these units have high sensitivity. The smaller ones have an effective time constant of approximately three milliseconds. Methods for producing them in quantity have been developed.

Another bolometer was developed at Johns Hopkins University by Professor Andrews and his associates. Made of columbium nitride, it operates at a temperature close to 15° A. in the region of transition to the superconducting state of this material. The bolometer has to be mounted in a vacuum chamber in a cryostat which contains liquid nitrogen and liquid hydrogen. In addition, marked advances were made in the production of metal strip bolometers, particularly nickel strip bolometers produced by various evaporation processes.

The outstanding development in radiometers is an outgrowth of the well-known Hays cell and consists of a gas-filled unit containing an absorber of thermal radiation which enters through a rock salt window. Another wall of the cell is made of a distensible film which changes its curvature upon a change in pressure of the gas in the cell and permits the detection of radiation.

Here and There in the Trade Literature[1]

THE *Bakelite Review* tells a story of engrossing interest in "The standby fleet":

America has a sleeping giant—ships, whose guns had been pointed toward Kwajalein and Luzon, Salerno and "Omaha" Beach in war, are not destined for the scrap pile in peace. Instead, in the current decommissioning program of the East Coast's Sixteenth Fleet and the West Coast's Nineteenth Fleet, over 2000 units of the U. S. Navy are being "packaged" against time and the elements in Vinylite plastics.

Guns and critical parts of the superstructure of these ships have been covered, *in place*, by spraying with the coating solutions. These impervious coverings are resistant to air, water, and corrosive agents and will preserve the valuable equipment for possible future need.

● "Rubber scientists robbed the baby's nursery" according to the April *Merck Review*.

For years, Zinc Stearate has been accepted by mothers all over the country as an excellent preventive for baby's chaffing. Its well-know water-resistant qualities have made Zinc Stearate . . . a household favorite. But who would have thought of using it to make a synthetic rubber?

Back in 1941 when scientists from the Standard Oil Development Company were struggling to bring synthetic rubber out of the laboratories into the factory, one of the biggest stumbling blocks to the mass production of Butyl rubber was the annoying teedency of the sticky raw masses to agglomerate and clog during the finishing processes. . . . Chemists and engineers racked their brains on this stopper—until one day they hit upon the idea of using Zinc Stearate to prevent uncontrolled conglomeration of the rubber particles.

● The following is from the April *Westinghouse Newsfront:*

MODELLED IN WAX

From gold inlays and fancy earrings to sleek blades for gas turbines—that's a thumbnail history of an ingenious method for forming complex shapes in metal. Called the "lost wax casting method," it has been used by dentists for 50 years and by jewelers for almost that long. More recently the Austenal Laboratories, Inc., of New York City applied the method industrially to the casting of high melting-point alloys. And now Westinghouse engineers are using it for the shaping of turbine blades and for other uses.

The lost wax method gets its name from the fact that the wax is really "liquidated" once it has done its job. First, wax replicas of the shape desired are made in much the same way that a dentist makes an impression of a tooth cavity. This replica is surrounded by a concrete-like mixture that hardens into a mold capable of standing up under very high temperatures. The hardened mold is heated to burn out the wax, leaving a cavity having the exact size and shape of the part to be cast. Into this cavity molten metal is poured and allowed to cool, after which the finished piece is removed by breaking away the mold.

The casting of gas turbine blades is a good example of the lost wax method at work. Because such blades must be capable of withstanding temperatures as high as 1500°F., they are made of special alloys, some of which are so hard that it is next to impossible to hammer them into shape in a forge shop or to machine them to the required tolerances. By making wax models of the blades, however, they can be cast in one operation which reproduces their complicated shape perfectly.

The lost wax method should also prove useful for the casting of small stainless steel pipe fittings, parts for lamp machines or business machines, instrument frames, and certain kinds of dies. Wherever forging or machining is impossible or too expensive—or wherever curved shapes or fine detail in metal parts are required—this old method with a new application may well prove the answer manufacturers have been looking for.

● Chemical products are coming from wood in greater and greater profusion. This industry is becoming particularly important in the South and is described in some detail in the April *Lion Oil News*. The following excerpts are representative:

Wood impregnated with certain chemicals can be made pliable and workable as putty. "Uralloy" can be kneaded, tied into knots, and bent into any shape desired. A remarkable feature is that, upon drying, uralloy retains the shape into which it was fashioned and becomes almost as hard as iron. Boat keels, furniture of unusual design, light fixtures, and specially shaped building beams are but a few of the curved wooden objects which can be manufactured from this product of wood chemistry. . . .

In paper manufacture, the only part of the wood necessary is the cellulose. The other component, the adhesive which holds the cellulose fibers together in the original tree, is lignin. Lignin is known as the "Black Knight of Chemistry"—its composition mystifies laboratory experts. But, despite their inability to fathom its makeup, scientists have developed thousands of products from this wonder-producing adhesive of Nature. These products are the wood plastics which may be seen on every hand all over the world. . . .

Wood sugar, although not as sweet, possesses nutritional qualities similar to those of cane and beet sugar. Not only wood alcohol, but ethyl or "grain" alcohol, is produced from trees. Live-

[1] For the company and address of a magazine cited, see THIS JOURNAL, January, 1946, p. 38.

stock feed and fertilizer are made from sawdust. Sawdust is also pressed into bricks to be used for fuel. Although not as practical as petroleum products, gases from wood and charcoal have been utilized as the power source for automobiles in some regions where gasoline was not abundant.

● As a preview to Dr. Sampey's "View of Africa" in the July issue of THIS JOURNAL, you will enjoy "Light for the dark continent" in the April *Service*.

Imagine a continent bigger than North America and South America put in one, a continent whose total current petroleum production would not fulfill the minimum power needs of one medium-sized American town.

That is Africa. In soils, timbers, enchanting places, breathtakingly beautiful scenery, and potential resources, Africa is the most richly endowed of all the continents.

But calling Africa the "Dark Continent" is much more than poetic whimsy. It is too literally true. Uncensused millions of African homes (known as *huts* to the membership of the Explorers' Club) are pitch-dark at night simply because when the moon doesn't shine, they have no light. Millions of square miles of Africa, particularly in the vast equatorial belt, are without roads primarily because there is no motor fuel available at prices that the people can afford to pay. . . .

Experts insist that, given sufficient fuel for light and power and lubricants for modern machinery, Africa could support at least one-third of all the peoples of the earth. Be that as it may, it seems doomed to remain a huge have-not in terms of petroleum supply. This in turn means that unless a great deal is done about it, Africa will remain the Dark Continent for a long time, if not indefinitely.

● We've never seen such fine color pictures of jet-propulsion engines as those in the April *Steelways*. Also, "Oil that grows on trees" tells about palm oil and its use in steel-rolling mills, while "Peppered with salt" has to do with steel mills also—the removal of scale from steel plate.

● Scholarly Noah Webster made at least one unscholarly error in his famous "American Dictionary of the English Language." He defined gelatin as "made from hoofs and horns." The gelatin industry, important and proud, suffered from an inferiority complex for a long while afterward. . . .

Contrary to Webster's original definition, gelatin is not made from hoofs and horns. It is a product obtained by the partial hydrolysis of collagen, a substance derived from the skins, white connective tissues, and bones of animals.

Thus begins "The emancipation of gelatin" in the April *Crown*.

● For a good elementary account of petroleum cracking and its relation to the production of high-powered motor fuel, see "Arranging atoms for tailormade molecules" in the April *Pure Oil News*. It contains good flow-sheets of liquid phase, vapor phase, and catalytic processes.

● The use of alpha-naphthylthiourea (ANTU for short) as a rat killer is described in the April-May *Du Pont Magazine*.

It all started as a part of Dr. Richter's research in the Phipps Psychiatric Clinic at Johns Hopkins. In this work Dr. Richter was attempting to determine the difference in taste desires of human beings based on heredity as well as other factors. Preliminary work in these studies is often carried out with rats since rats have the peculiar ability of being able to determine or select nourishing foods and avoid poisonous substances.

During the course of one of these tests Dr. Richter fed to the rats a chemical which had frequently been used for taste tests in humans. This chemical, phenyl-thiourea, which to some people tastes bitter while to others it is tasteless, was the beginning of the whole story of ANTU. The day following the tests with this chemical all of the rats used in the test were dead. Imagine the surprise of the investigators who had previously felt, as a result of their work with humans, that this chemical was nonpoisonous. Accidents will happen, but it is the wise investigator like Dr. Richter who makes the most of a such a situation. . . .

As he continued his work, Dr. Richter found the laboratory rats would eat enough of the chemical to poison themselves, but that wild rats trapped on the city dumps of Baltimore apparently objected to the bitter taste of phenyl-thiourea and consequently would not eat bait which had been treated with the chemical.

To Dr. Richter this situation raised the possibility of using chemicals which might be related to phenyl-thiourea, but which would not have the objectionable bitter taste. He appealed to the Du Pont Company for a supply of related materials, knowing that such materials might be available from the Du Pont laboratory file for his investigations. Twenty-four different but related compounds, first and second cousins to phenyl-thiourea, were selected from the chemical files and sent to Dr. Richter for further investigations. Of these 24, No. 15 on the list was ANTU, the one which is now recognized as an outstanding rodenticide.

● The following items are from the March *Aminco Laboratory News:*

A new type of small powerful magnet, made of iron rust and cobalt oxide and claimed to be the lightest magnet ever developed, was recently announced by the General Electric Company. It has been used in highly sensitive aircraft meters and other wartime devices and is now available for civilian use.

The rust used in making the magnet is actually an iron oxide ore in which the oxide is chemically the same as iron rust.

The new type of magnet is a nonconductor of electricity and is not easily demagnetized; thus it may be used in high-frequency magnetic fields with little eddy current loss. . . .

A new heat-absorbing color-transmitting glass announced by the American Optical Company, Southbridge, Massachusetts, permits motion and still pictures to be projected in their original colors, and movie and television actors to be protected from the intense heat of the spotlights and floodlights.

In projectors, the new glass serves as a screen to absorb the heat emitted by the light source, thus protecting films and slides from damage or burning. It will fully protect a film if the projector is stopped to permit the study of a particular scene as a still picture on the screen.

The glass absorbs approximately 90 per cent of the infrared (heat) radiation and transmits about 85 per cent of the light. This is a high transmission because approximately eight per cent is always lost by reflection.

The new product is formed from carefully balanced parts of phosphorus, aluminum, and silicon oxides, supplemented by various conditioning ingredients, together with ferrous oxide as the heat-absorbing agent. It is chemically stable, and can be molded, ground, polished, and fabricated like ordinary glass. . . .

Another new type of glass, in which beryllium fluoride is substituted for the silicon dioxide (ordinary sand) used in conventional glass formulae, lets light go through at a higher speed than any other known glass. The light velocity is 146,000 miles a second as compared with 122,000 miles a second in the kind of glass used in spectacles. . . .

As a result of studies made by W. Colbert of Pennsylvania State College and N. J. Kreidl of the Bausch & Lomb Company, several series of new and unusual uranium colors were obtained, one of which exhibits a truly red color. Hitherto, red colors were obtainable only in glasses of the gold, copper, antimony, sulfide, and cadmium sulfoselenide ruby type. The new red uranium glass has color centers which are ionic in character and therefore remain unaffected by thermal treatment; consequently, the new red glass is strictly reproducible.

Odor and the Organic Chemist

EVERETT L. SAUL

Felton Chemical Company, Inc., Brooklyn, New York

TO MANY organic chemists and particularly to students of organic chemistry, odor consciousness has been limited to isolated chemicals possessing to a high degree some particularly disagreeable and obnoxious characteristics. The mercaptans, scatol, the amines, etc., have been widely advertised as powerful disturbers of the olfactory sense. Little if any attempt, however, has been made to make the student aware of association of chemicals and odor. Indeed, odor has been looked upon as more or less of an anomalous or purely incidental property of organic substances.

To realize the importance of odor it may be quite needless to mention the fact that a few billion dollars are expended annually in the United States alone on the purchase of cosmetic preparations whose successful sale often hinges on their odor appeal. Every ounce of soap, skin cream, sachet, hair preparation, bath preparation, household insecticide, furniture polish, shoe polish, kitchen "deodorizer," to list only a few, contains a small percentage of a mixture of chemicals whose sole claim for such application resides in the fact that they have odors.

The art of recognizing, identifying, classifying, and choosing chemicals on the basis of odor has been put almost exclusively in the hands of a comparatively few highly specialized men known as perfumers. Some of these perfumers have but a limited knowledge of organic chemistry and its method of procedure. And yet, from experience alone they are able to distinguish hundreds of hydrocarbons, alcohols, aldehydes, esters, etc., or types, not by what we know as "scientific methods," but by smelling them!

It must first be emphasized that odor is as much a property of a chemical as is color, melting point, density, etc. The fact that a pure chemical is odorless is often as important as that it possesses a distinctive and powerful aroma. Unfortunately the sense of smell lacks the precision attained by less subjective means of determining attributes of chemicals. Perhaps the future will perfect a method of accurately and objectively describing odors and their intensities.

The resourceful and imaginative scientific worker does not forego the opportunity of accepting and capitalizing on any clues concerning the nature of the material he may be investigating. During his research on carotene and vitamin A, Paul Karrer recognized the presence of ionone by its odor only. This shortened the work of establishing the structure and hastened the ultimate synthesis of this vital accessory food factor. How fortunate it was that the ionones had been synthesized some 40 years before by Tiemann who had interested himself in the perfume of the violet!

Another giant of organic chemistry, Leopold Ruzicka, through his keen appreciation of the phenomena of odors, showed us that our notions about the size of ring structures and stability had to be revised when he disclosed the 15 and 17 carbon atom rings of muscone and civetone. Even one of the sterols, he claims, has a musk odor. On the other hand, Ruzicka, working with Staudinger on the chemistry of pyrethrin, failed to mention the powerful odor of dihydrojasmone although he later claims to have discovered its perfume value.

During the preparation of organic chemicals the chemist should be forever on the alert for odors, foreign or novel, which may help him to identify impurities or indicate the presence of some new compound. Time and effort may be conserved if the chemist can recognize odors which may immediately indicate the direction of his subsequent research on purification and isolation. How many chemicals are buried in the masses of scientific literature, awaiting a deserved place in the roster of perfume chemicals? The situation is as unfortunate as when the chemist reads an article on a dye, to find everything explained in detail, but no mention made of color.

What odors are of interest to a perfumer, I venture to say, is almost impossible for a chemist to predict. The good perfumer has often startled us by his choices. What shall we say of the alkyl substituted quinolines and the indols, the alpha alkyl substituted cinnamic aldehydes, trichlormethyl phenyl carbinyl acetate, the macrocyclic esters, diphenyl methane, octinoic acid methyl ester, etc., to mention a few of the purely synthetic chemicals he has utilized? There also arises the question of how to describe the odors of new chemicals. Even when by good fortune the odor of a new substance is reminiscent of that of a flower, such as a rose, violet, or lily, the problem is still only half solved. What remains to be said involves nuances, and at this point the difficulties of language seem almost insurmountable. The perfumer uses such terms as sweet, woody, powdery, green, leafy, musty, harsh, earthy, tarry, etc., and by a casual consideration of these terms it is clear that they are highly inadequate adjectives because they are not precise. The word "sweet," for example, means for all of us the well-defined sense of taste of cane sugar; but the sugars are odorless, and we must now learn to think of vanillin as having a sweet odor. The pure taste sensation stimulated by vanillin is that of bitterness. To say that geraniol is sweeter than citronellol or phenylethyl alcohol sweeter than phenylpropyl alcohol, a new concept must be learned. But this qualitative distinction of the so-called sweetness exists to a large extent in the imagination of the perfumer. What I mean to infer is not that the perfumer cannot detect these subtle differences in the odor of chemicals, but

rather that his choice of describing them is subjective, arbitrary, and inadequate. "Woody" may conjure the odor of cedar to some, poplar to others, and birch to still others. Surely the "leafy" odor of peppermint, geranium, hedge, and hemlock does not convey a single general sensation to the nose. These are awkward words, but they are the best we know and possess at least some value.

At the moment, accurate descriptions are impossible, but we must to the best of our ability translate our odor impressions to our fellow chemists. Certainly there is less harm done by inadequately describing an odor than by omitting to mention it at all. For the sake of simplicity it is best to do this by reference to well-known substances or odor complexes. This is at least practical because we are familiar with the floral and flavor complexes and because the types of perfume chemicals are legion.

For reference substances the author recommends the commonly known and generally experienced odors which, when used as the prototypes, have at least the possiblity of being recognized by all of us. These substances would include the flower, spice, fruit, animal, and vegetable odors, kerosene, turpentine, gasoline, naphthalene, camphor, cedar (pencil), tar, nitrobenzene (shoe polish), amyl acetate (banana oil), pine, butter, etc. For instance we might immediately think of rose, hyacinth, lily, gardenia, lilac as floral odors; apple, pear, peach, orange, lemon, and pineapple as fruit odors; spearmint, peppermint, wintergreen, cinnamon, clove, dill, anise, or vanilla as spice odors; raspberry, currant, and blackberry as berry odors; bitter almond as a nut odor. The reference substances may be clarified in further detail by listing the known ingredients which compose the original complex, as follows:

Rose—geraniol, citronellol, phenyl alcohol
Lemon—citral, limonene
Wintergreen—methyl salicylate

It is important and informative to indicate whether a chemical possesses an agreeable or disagreeable odor and also to attempt to estimate its intensity quantitatively. A chemical may be very powerful in odor, or weak, or lasting, or evanescent. The persistence or volatility of a chemical in relation to its odor may often be predicted on the basis of such physical properties as its vapor pressure or boiling point. Odor intensity seems to be to a large extent a physiological phenomenon associated with some chemical reaction occurring at the locus of the olfactory stimulation.

The chemist should be made aware of and practice the qualitative sort of distillation at atmospheric pressure which is universally employed by the perfumer. The distillation equipment of the perfumer consists simply of a container of so-called smelling blotters. With this simple apparatus he has become highly skilled and proficient. He places a few milligrams of a perfume or chemical, or a dilute solution of them, in some solvent such as alcohol, on the end of a smelling-blotter and wafts it under his nose. He tries to recognize the constitutents as they evaporate from the blotter. In the case of a chemical the odor should remain constant from the first moment to the last, when it has just escaped in the form of vapor from the blotter. Traces of odoriferous impurities are often readily detected by this method when all others fail. In some cases a blotter must be studied for a week or more.

It may be of some interest to the chemist who has synthesized a new chemical and found it pleasantly odoriferous to mail a very small sample to some perfume manufacturing company for inspection. The perfumer will welcome a prospective, novel, and useful odor and will attempt to analyze its aroma value for the chemist. Such cooperation may be of mutual benefit to the perfumer and the organic chemist.

Perhaps I should add here a note of caution for the organic chemist. Because he is in most cases unfamiliar with the perfume value of the chemicals available to the perfumer, the chemist may find results occasionally discouraging by the rejection of many or most of the odors which he considers unusual or intriguing. For example, isoamyl salicylate finds a wide application in many of the cheaper types of perfumes. Let us imagine that the *n*-hexyl ester had never been prepared. Some chemist, having produced it for the first time, finds its odor pleasant and suggestive and hopefully submits a sample to the perfumer. The latter agrees that the odor is pleasant but so similar in character to that of isoamyl salicylate that the extra cost of the *n*-hexyl ester is not justified.

After most of our wars, U. S. armies quickly became collections of civilians eager to get home and not too interested in the country's future military or foreign policy needs. The same old American custom underlies the actions of overseas Yanks now. It may not do for the year 1946—if it produces a public opinion which prevents the U. S. from playing the strong role required of it in world affairs.

Separation and Identification of Cobalt, Nickel, Zinc, and Manganese

R. K. McALPINE

University of Michigan, Ann Arbor, Michigan

THE scheme that has been used at the University of Michigan for the separation of the common metals into groups for qualitative analysis is based on the use of HCl for Group I, H_2S in slightly acid solution for Group II, NH_4OH in slight excess in the presence of a high concentration of NH_4Cl for Group III, H_2S in an ammoniacal solution for Group IV, and $(NH_4)_2CO_3$ for Group V. The difficulties in the separation of Group III from Group IV by this scheme are recognized; but practical experience has shown that with proper attention to certain specific details in the procedure, there is no serious difficulty in identifying small amounts of each of the metals in these two groups in the presence of fairly large amounts of the other metals. Further, the simplicity of presenting this method to the student has had its weight in leading to a retention of this scheme.

This procedure places the four metals cobalt, nickel, zinc, and manganese in Group IV. The method of separation and identification which has been employed involves, briefly, treatment of the precipitated sulfides with cold 1 *N* HCl to dissolve the ZnS and MnS, leaving CoS and NiS to be dissolved in HCl + HNO_3. Separate portions of the solution of $CoCl_2$ and $NiCl_2$ are tested individually for cobalt with concentrated NH_4-CNS and amyl alcohol, and for nickel with ammonium hydroxide and dimethyl glyoxime. The solution containing $ZnCl_2$ and $MnCl_2$ is boiled to remove H_2S, then treated with excess NaOH and bromine water, precipitating the manganese as MnO_2 and leaving zinc in solution as Na_2ZnO_2. The MnO_2 is filtered out, dissolved in HNO_3 + H_2O_2, and treated with a strong oxidizing agent to convert any manganese to $HMnO_4$. The solution of Na_2ZnO_2 is treated with a little NH_4OH to reduce any excess of hypobromite; then H_2S is passed in to precipitate the zinc as ZnS.

In the laboratory the student finds this procedure somewhat unsatisfactory for the following reasons: (*a*) since freshly precipitated cobalt and nickel sulfides, even after short standing, dissolve slowly in cold, 1 *N* HCl, significant fractions of these metals may go into solution along with $MnCl_2$ and $ZnCl_2$; (*b*) any cobalt or nickel in the solution will give a black precipitate of NiO_2 or $Co(OH)_3$ where MnO_2 is expected and thus interfere with estimating the amount of manganese in terms of the volume of MnO_2 precipitated; (*c*) if the $MnCl_2$-$ZnCl_2$ solution contains appreciable amounts of NH_4^+ (from incomplete washing of the group precipitate or from the use of ammonium salts in the wash water), the bromine added may be reduced by the NH_3 in the alkaline solution without oxidizing and precipitating the manganese, cobalt, or nickel as expected; (*d*) with excess of bromine water, in the presence of cobalt as catalyst, small amounts of manganese may be oxidized beyond MnO_2 to form some manganate or permanganate in the solution; (*e*) the cobalt and nickel sulfides, left after separation from manganese and zinc, have changed to the more insoluble modifications and the reaction with HCl + HNO_3 requires boiling for a little while to dissolve these precipitates effectively; and (*f*) cobalt interferes with the recognition of small amounts of nickel by the direct test with dimethyl glyoxime; and in spite of the statement in the literature and in many texts that in such a case it is onyl necessary to use a larger amount of the reagent, the experience in this laboratory shows that in the ordinary small volume in which the test is made, the use of excess of dimethyl glyoxime does not effectively identify small amounts of nickel in the presence of moderately large amounts of cobalt.

With these difficulties in mind it seemed an interesting exercise to attempt to devise an alternative method for the separation of these metals that would give cleaner separations and would permit a simpler estimation of the relative amounts of the different metals present.

The procedure that was finally set up for experimental study started with dissolving all the sulfides in HCl + HNO_3, making strongly ammoniacal, and adding an oxidizing agent which would simultaneously precipitate any manganese as MnO_2 and oxidize the cobaltous ammonia ion to the much more stable cobaltic ammonia form. After filtering out the MnO_2, the cool filtrate could then be treated with excess of NaOH (considerably more than equivalent to any ammonium salts present), which would precipitate the nickel as $Ni(OH)_2$ or NiO_2 according to the strength of the oxidizing agent used, leaving the cobalt in solution as the cobaltic ammonia form and the zinc as the zincate. After filtering off the nickel precipitate, the filtrate could then be boiled to decompose the cobaltic ammonia ion and precipitate the cobalt as $Co(OH)_3$, leaving the zinc still in solution. After filtering out the $Co(OH)_3$, the filtrate could be tested for zinc by passing in H_2S. The individual precipitates of MnO_2, $Ni(OH)_2$, and $Co(OH)_3$ could be dissolved separately in HNO_3 + H_2O_2 and tests applied on these solutions to identify the individual metals and to judge the relative amounts present.

Preliminary experiments were run using 20 ml. of a stock solution containing all four metals in such concentrations that 50 mg. of each was present in the sam-

ple taken. The preliminary precipitation and dissolving of the sulfides was omitted. To the solution was added 5 ml. of 5 *N* NH_4Cl, 10 ml. of 5 *N* NH_4OH, and 5 ml. of a 5 per cent solution of sodium hypochlorite (commercially available in the form of Roman Cleanser).[1] The solution was warmed slightly (approximately 45° C.) and let stand four to five minutes for precipitation. The brown precipitate of MnO_2 was filtered out, washed, and set aside for later testing. The filtrate was cooled to room temperature and treated with 15 ml. of 3 *N* NaOH. A tan colored precipitate formed, consisting of $Ni(OH)_2$ and a little MnO_2. This was also set aside for further testing. On heating the filtrate nearly to boiling, a black precipitate of $Co(OH)_3$ started to form, but it was necessary to boil the solution three to four minutes before the precipitation was complete. This precipitate was very finely divided, showing a tendency to run through the filter paper and to clog the filter. The use of filter paper pulp improved this situation. The filtrate was carefully examined, and if there were any suspicion of pink or tan color, it was boiled again for a short time and refiltered. When the filtrate was perfectly clear and showed no sign of darkening on heating, it was tested for zinc by passing in H_2S. The precipitate of zinc sulfide was a clean white in considerable contrast to the gray precipitate frequently seen in the laboratory. The precipitate of $Co(OH)_3$ was washed and set aside for further testing. The precipitate of MnO_2 was dissolved in 5 ml. of 5 *N* HNO_3 + 1 ml. of H_2O_2 (3 per cent solution). To test for manganese, this solution was poured into a clean test tube and the two or three drops remaining in the original tube used for the test. On adding 3 to 4 ml. of 5 *N* HNO_3 and 0.1 to 0.2 g. of $NaBiO_3$ and shaking thoroughly, the excess $NaBiO_3$ was permitted to settle and the color of the solution observed. A fairly deep permanganate color was noted. To test for possible carrying down of nickel, 1 ml. of the $Mn(NO_3)_2$ solution was made alkaline with NH_4OH, then slightly acid with $HC_2H_3O_2$, and a few drops of H_2O_2 added to reduce the MnO_2. Next 1 to 2 ml. of dimethyl glyoxime reagent was added, but no precipitate formed, showing that no nickel had been carried down by the original manganese precipitate. Another portion of the solution (1 to 2 ml.) was tested for Co^{++} by adding 3 to 4 ml. of a 50 per cent solution of NH_4CNS and a half inch layer of amyl alcohol. After shaking thoroughly and letting the alcohol layer form again, a light green color was noted. On adding a drop of $SnCl_2$ reagent to reduce the trace of $Fe(CNS)_3$, a faint blue color was seen, showing that a very small amount of cobalt had been filtered out along with the manganese.

The precipitate of $Ni(OH)_2$ (plus MnO_2) was dissolved in 5 ml. of 5 *N* HNO_3 + 1 ml. of H_2O_2. The test for nickel was applied by taking two to three drops of the solution in the same way as with the manganese solution, adding 2 to 3 ml. of water, 1 ml. of 5 *N* NH_4OH, and 1 to 2 ml. of dimethyl glyoxime. A bulky scarlet precipitate formed, darkened by the presence of a little MnO_2. To remove the latter, the solution was made moderately acid with $HC_2H_3O_2$ and a few drops of H_2O_2 added. The bright scarlet precipitate of the nickel salt remained. A test for manganese was applied by using about 0.5 ml. of the solution and oxidizing with HNO_3 and $NaBiO_3$. A moderate depth of color of $HMnO_4$ was obtained, showing that a significant amount of the manganese had escaped earlier precipitation and had been carried down with the $Ni(OH)_2$. Another portion was tested for cobalt, giving a faint positive test, showing that a very small amount of cobalt had been filtered out with the $Ni(OH)_2$.

The precipitate of $Co(OH)_3$ was dissolved in a mixture of HNO_3 and H_2O_2, the reaction being somewhat slow and requiring the application of heat. By heating the reagent nearly to boiling and pouring it through the filter paper two or three times, the precipitate was dissolved effectively. Tests were applied for manganese and nickel with negative results, while two or three drops of the solution gave a strong test for cobalt with NH_4CNS and amyl alcohol.

After the procedure had been studied with all four metals present in moderate amounts, it was next applied to each of the metals separately. Thus 50 mg. of Mn^{++} in 20 ml. volume was treated with 5 ml. of 5 *N* NH_4Cl, 10 ml. of 5 *N* NH_4OH, and 5 ml. of 5 per cent sodium hypochlorite reagent, warmed to 45–50°, and let stand about five minutes. The brown precipitate was filtered out and the filtrate put through the successive operations that were used to precipitate nickel, cobalt, and zinc. A small precipitate was obtained when excess of NaOH was added. Judging by relative volumes, about 95 per cent of the manganese was removed in the first precipitation, leaving 5 per cent to be precipitated when the alkalinity was increased. After filtering the cool solution, no further precipitate was obtained on boiling or on treating the final solution with H_2S.

When 50 mg. of nickel was carried through the whole procedure, no precipitate was obtained by oxidation in the ammoniacal solution; a gelatinous, green precipitate formed when excess NaOH was added to the cold solution; no further precipitate formed on heating the filtrate to boiling; and when H_2S was passed in, no visible precipitate formed although a very slight darkening of the solution took place. Similar experiments with 50 mg. of cobalt gave no precipitate on oxidation in ammoniacal solution and no precipitate on stirring excess of NaOH into the cold solution. On heating to boiling, filtering, boiling again, and refiltering until the solution was colorless, no precipitate was obtained with H_2S although a faint darkening occurred as in the case of nickel.

A third set of tests was run with all four metals present, but in smaller amounts—namely, 5 mg. of each.

[1] Experiments were tried also with hydrogen peroxide and with potassium persulfate as oxidizing agents. The reactions with the different reagents were so varied that they are being reported in the following paper under the title, "The anomalous behavior of some oxidizing agents," on page 301, THIS JOURNAL.

In this case most of the manganese precipitated with the nickel, although sufficient was obtained in the initial oxidation to give a good permanganate color when 2 ml. of the final solution of $Mn(NO_3)_2$ was oxidized. The nickel hydroxide precipitated normally, carrying down the rest of the manganese when excess NaOH was added; the cobalt precipitated when the solution was boiled, and the zinc gave a small white precipitate when H_2S was passed into the final solution.

A fourth set of tests was run to check the accuracy of separation of 5 mg. of each of the earlier metals in the scheme from 50 mg. portions of each of the later metals. Again the manganese precipitated very incompletely in the first step, the balance coming down with the $Ni(OH)_2$. The 5 mg. of nickel precipitated readily with the NaOH in the presence of 50 mg. each of cobalt and zinc. Also the 5 mg. of cobalt precipitated as readily as usual in the presence of 50 mg. of zinc.

In the fifth set of tests 5 mg. of each of the later metals in the scheme were tried in the presence of 50 mg. portions of the earlier metals. After precipitating 50 mg. each of Mn, Ni, and Co, the 5 mg. of zinc gave a faint but recognizable precipitate with H_2S. Apparently somewhere near half the zinc was lost with the earlier precipitates. Five mg. of cobalt gave a normal precipitate of $Co(OH)_3$ after removal of 50 mg. each of Mn and Ni. In the case of 5 mg. of nickel the precipitate appeared unduly large because of the presence of the manganese incompletely removed earlier.

A summary of the advantages of this alternative procedure may be made as follows: (*a*) all the metals are separated from each other before the confirmatory tests are applied, thus making it simpler to judge the relative amounts of the individual metals; (*b*) in the confirmatory test for cobalt with NH_4CNS the color in the amyl alcohol layer is a clearer blue than that frequently encountered in the other procedure where a trace of ferric iron is more apt to be present; (*c*) in the final test for zinc the precipitate is typically white instead of gray or black; and (*d*) an opportunity is given to discuss in class some of the principles of oxidation and reduction in greater detail, while the extreme stability of the cobaltic ammonia ion calls attention to the importance of the cobalt complexes in the earlier experimental studies of coordination compounds.

The main difficulties encountered in the procedure are: (*a*) since the manganese is not fully precipitated in the first step, in testing for small amounts of this metal it is necessary to apply the test also on the solution of nickel nitrate to estimate the total amount of manganese present; (*b*) the precipitate of $Co(OH)_3$ forms slowly and in very finely divided form so it is necessary to use a filter aid and to boil the solution repeatedly to make sure the cobalt is completely removed before testing for zinc with H_2S; (*c*) occasionally in the precipitation of $Co(OH)_3$ a blue filtrate is obtained. This involves the presence of a little cobalt in the bivalent state and is easily remedied by adding a few drops of H_2O_2 and boiling again. As the cobalt is oxidized, it precipitates readily.

STAMP RECONSTRUCTION?

Recently an Ultramarine and Dyestuff representative of the Calco Chemical Division, American Cyanamid Company, while on a business trip in South America, acquired one of the most rare Brazilian stamps, the black 600 unused of the Inclinado Empire Series issued in 1844–46. This stamp had been purchased from a Chilean dealer and was from the Alessandri Collection in Santiago, Chile.

In showing this stamp to a New York dealer, it was questioned whether the stamp had been reconstructed in one corner because when put into benzene, this corner appeared different from the others. Careful examination under the microscope by various methods of illumination, including ultraviolet light, could not show this corner to be different. Paper fibers ran directly from the center of the stamp into the questioned corner, making a repair quite improbable.

However, the most convincing observation to prove the authenticity of the stamp oddly enough came back to Ultramarine Blue Pigment. The microscope at high magnification revealed a clear and rather large-size transparent blue pigment throughout the paper, both in the body of the stamp and in the questioned corner. It is probable that the paper on which the stamp was printed was of French origin and that the Ultramarine had been added to "whiten" the paper. The corner which had failed to "wet out" in the benzene was probably caused by a hard spot produced by the reaction of some chemical dropped upon the paper or due to some mechanical difference in the construction of the original paper. Thus, the Ultramarine pigment put in by the artisan years ago made it possible to establish the identity of very small portions of his paper today.

Anomalous Behavior of Some Oxidizing Agents

R. K. McALPINE

University of Michigan, Ann Arbor, Michigan

A NEW method has just been worked out for the qualitative separation of manganese, nickel, cobalt, and zinc in an ammoniacal solution. (See page 298, THIS JOURNAL.) The manganese is precipitated by an oxidizing agent which at the same time oxidizes the cobaltous ammonia ion to the more stable cobaltic ammonia form. To the cool filtrate from the manganese dioxide is added an excess of sodium hydroxide, precipitating the nickel as hydroxide. The filtrate from the nickel hydroxide is boiled to precipitate the cobalt as cobaltic hydroxide, leaving zinc in solution as sodium zincate to be tested for with H_2S.

In the experimental studies three different oxidizing agents were tried, and the differences in the results obtained are responsible for the title of this paper. The oxidizing agents were (1) a five per cent solution of sodium hypochlorite in the form of a fresh bottle of "Roman Cleanser," (2) a three per cent solution of hydrogen peroxide, the usual commercial preparation which is stabilized by acetanilide, and (3) potassium persulfate, added as a solid or as a saturated aqueous solution. The approximate normalities of the three reagents were NaClO = 1.3 *N*, H_2O_2 = 1.7 *N*, and $K_2S_2O_8$ (saturated solution) = 0.3 *N*. In the actual oxidations of manganese and cobalt the volume was approximately 40 ml. with 5 ml. of 5 *N* NH_4Cl and 10 ml. of 5 *N* NH_4OH present, giving a pH of approximately 9.

The normal oxidation potentials of these oxidizing agents and the corresponding half reactions have been taken from Latimer's book, "Oxidation Potentials," with signs and equations reversed.

$$E_0 S_2O_8^{--}/SO_4^{--} = 2.05\ (S_2O_8^{--} + 2\epsilon^- = 2SO_4^{--})$$

$$E_0 ClO^-/Cl^-, \text{ basic solution} = 0.94\ (ClO^- + H_2O + 2\epsilon^- = Cl^- + 2OH^-)$$

$$E_0 H_2O_2/H_2O, \text{ basic solution} = 0.87\ (HO_2^- + H_2O + 2\epsilon^- = 3OH^-)$$

From the half reactions one would judge that the strength of the persulfate as an oxidizing agent would not be affected by a change in the alkalinity of the solution. In the other two cases, however, the change in concentration of hydroxyl ion from 1 *M* (standard conditions) to 1×10^{-5} should increase the strength of these oxidizing agents since hydroxyl ion is a product of the reduction. The usual type of calculation shows that at a pH of 9 the oxidation potential of the hypochlorite should rise to approximately 1.24 volts and that of hydrogen peroxide to approximately 1.31 volts. From these data one would judge the persulfate to be much the strongest oxidizing agent of the three, the other two being fairly strong oxidizing agents, with hydrogen peroxide slightly the stronger of the two.

The reducing agents to be oxidized are manganous ion, cobaltous ammonia ion, and possibly nickelous hydroxide (if excess of the oxidizing agent is still present when the sodium hydroxide is added). Referring again to Latimer and changing the data to oxidation potentials of the oxidized forms, one finds:

$$E_0(Co(NH_3)_6^{+++}/Co(NH_3)_6^{++}) = 0.1\ (Co(NH_3)_6^{+++} + \epsilon^- = Co(NH_3)_6^{++})$$

$$E_0(Mn(OH)_3/Mn(OH)_2) = -0.4\ (Mn(OH)_3 + \epsilon^- = Mn(OH)_2 + OH^-)$$

$$E_0(MnO_2/Mn(OH)_3) = 0.5\ (MnO_2 + 2H_2O + 2\epsilon^- = Mn(OH)_3 + OH^-)$$

$$E_0(NiO_2/Ni(OH)_2) = 0.49\ (NiO_2 + 2H_2O + 2\epsilon^- = Ni(OH)_2 + 2OH^-)$$

On recalculating the values for $Mn(OH)_3$ and MnO_2 to the basis that the concentration of hydroxyl ion = 1×10^{-5}, the potentials become −0.10 and 0.80, respectively. The value for NiO_2 does not need to be changed appreciably since the concentration of hydroxyl ion is made approximately 0.4 *M* in the precipitation of the nickel.

From the above data it would appear that all three of the oxidizing agents are sufficiently powerful to oxidize Mn^{++} beyond $Mn(OH)_3$ to MnO_2, and to oxidize $Co(NH_3)_6^{++}$ to $Co(NH_3)_6^{+++}$ and $Ni(OH)_2$ to NiO_2. To test the readiness with which these reactions take place several sets of experiments were tried.

For the oxidation of manganese three identical solutions were set up in 8-inch test tubes, each containing 10 mg. of Mn^{++} (as $MnCl_2$), 5 ml. of 5 *N* NH_4Cl, and 10 ml. of 5 *N* NH_4OH in a total volume of 25 ml. To the first solution was added 5 ml. of the hydrogen peroxide reagent. A very dark brown precipitate formed instantly, and considerable frothing occurred as the excess of the reagent decomposed under the catalytic influence of the precipitate.

To the second solution was added 5 ml. of the saturated solution of potassium persulfate. No immediate reaction was observed, but after a minute or two the solution became a light tan, then gradually darkened with formation of a brown precipitate which later turned black.

To the third tube was added 5 ml. of the sodium hypochlorite solution. As in the case of the persulfate no immediate reaction was observed, but, within a minute or two the solution became a light brown. This darkened shortly to nearly black; then as the solution was swirled, it started to become lighter, most of the precipitate dissolving with development of a purple tinge in the solution. After perhaps five minutes there was a slight reddish brown precipitate in the solution looking quite a bit like ferric hydroxide. On longer standing the precipitate slowly increased in amount and became a darker brown.

On comparing the bulks of the three precipitates after the reaction with the persulfate appeared to be complete, the volume was largest in the case of the hydrogen peroxide reaction and smallest with the sodium hypochlorite. On filtering and testing the filtrates with excess sodium hydroxide, it was found that precipitation was quite complete with both hydrogen peroxide and potassium persulfate, but very incomplete in the case of sodium hypochlorite.

A summary of the results of this first series of reactions would state that the hydrogen peroxide oxidizes manganous ion very rapidly in an ammonium chloride-ammonium hydroxide solution, that potassium persulfate acts much more slowly, and that sodium hypochlorite shows an intermediate rate. The reactions seem to proceed smoothly to completion in the first two cases, but in the case of the sodium hypochlorite a curious irregularity is noted in that after the precipitate is once formed, it reverses itself and largely goes back into solution. This peculiar behavior of the sodium hypochlorite will be discussed at some length later. For the present, however, it will be interesting to compare the efficiency of these oxidizing agents on nickelous hydroxide.

Three solutions were set up each containing 50 mg. of nickel ion (as $NiCl_2$), in 15 ml., and 5 ml. of 3 *N* NaOH were added, precipitating light-green gelatinous nickel hydroxide. To the first tube was added 5 ml. of the saturated solution of potassium persulfate. Instantly the precipitate turned black due to oxidation to nickel dioxide. To the second tube was added 5 ml. of the sodium hypochlorite solution. The precipitate turned black very promptly although there appeared to be a slightly slower reaction than in the first case. To the third tube was added 5 ml. of the hydrogen peroxide solution. No change was observed. After standing about five minutes, an effervescence was noted, gradually increasing in amount and finally stopping. The gas evolved was oxygen, due to catalytic decomposition of the hydrogen peroxide by the nickelous hydroxide. The final precipitate in this tube was a little darker green than the original nickelous hydroxide, suggesting a slight surface oxidation to the dioxide.

In this second series of reactions the effectiveness of the three oxidizing agents is just the reverse of that noted in the first series. Potassium persulfate is the fastest of the three, with sodium hypochlorite a close second, while only a negligible amount of oxidation occurs with the hydrogen peroxide.

Since in the analytical procedure for which these reagents might be used the nickel would be precipitated from an ammoniacal solution by addition of excess of sodium hydroxide, it seemed worth while to repeat this experiment on the oxidation of the nickel hydroxide under different conditions. Three solutions were prepared, each containing 50 mg. of nickel, 5 ml. of 5 *N* NH_4Cl, and 10 ml. of 5 *N* NH_4OH in a total volume of 20 ml. Five ml. of the potassium persulfate reagent was added to the first solution, 5 ml. of sodium hypochlorite to the second, and 5 ml. of hydrogen peroxide to the third, and then each solution was treated with 15 ml. of 3 *N* NaOH. With the potassium persulfate a black precipitate of nickel dioxide formed instantly. In the case of the sodium hypochlorite a precipitate formed promptly, but it was the green nickelous hydroxide. With the third solution a green color developed immediately, but no precipitate formed. Thus in the presence of the ammonium hydroxide only the potassium persulfate oxidized the nickelous hydroxide to the dioxide and hydrogen peroxide showed the entirely unexpected property of keeping the nickelous hydroxide from precipitating. As this last solution stood for a short time, an effervescence started and gradually increased in amount. As this continued, the solution became cloudy and a dark green precipitate slowly formed. After about 10 or 15 minutes the nickel appeared to be quite fully precipitated as a slightly oxidized nickelous hydroxide; and on longer standing, the color became lighter as if the surface of dioxide were being reduced. The gas given off during the precipitation was tested and found to be oxygen.

Since the peptized condition of the nickelous hydroxide required the presence of some excess of hydrogen peroxide, it was an obvious experiment to try the effect of varying amounts of hydrogen peroxide with a given amount of nickel. Setting up three ammoniacal nickel solutions as before, approximately one equivalent of hydrogen peroxide was added to the first solution, two equivalents to the second, and three equivalents to the third; then each was treated with the usual excess of NaOH reagent. In the first solution the nickel precipitated readily as the hydroxide, in the second a precipitate formed immediately but considerably less than in the first case, and in the third solution no immediate precipitation occurred. In all three cases the catalytic decomposition of the hydrogen peroxide started in a minute or two; and as it proceeded, precipitation became more complete in the second solution and shortly started in the third.

In the presence of ammonium hydroxide two irregularities are noted: (1) the sodium hypochlorite does not oxidize the nickelous hydroxide to the dioxide, and (2) hydrogen peroxide not only fails to oxidize the nickelous hydroxide but actually peptizes the latter and prevents its normal precipitation. The first time this latter effect was observed the first guess was that a mistake had been made in measuring out the amounts of the various reagents and insufficient sodium hydroxide had been added. As the experiment was repeated, however, it quickly became evident that a new irregularity had been encountered.

The next comparison of the three oxidizing agents was made on a solution of cobaltous ammonia chloride. Three solutions were prepared, each containing 10 mg. of cobalt (as $CoCl_2$), 5 ml. of 5 *N* NH_4Cl, and 10 ml. of 5 *N* NH_4OH in a total volume of 25 ml. When 5 ml. of H_2O_2 was added to the first tube, the color changed quickly to a moderately deep red which persisted without further change. With the sodium hypochlorite the red color developed rather slowly, and there was a

recognizable difference between the two even after 15 minutes. With potassium persulfate the color shifted rather quickly to a greenish blue. On standing, a reddish tinge developed in the last solution, and in time this became identical with the color produced by the hydrogen peroxide. Thus in the case of cobaltous ammonia ion the oxidation proceeds most rapidly with hydrogen peroxide and most slowly with sodium hypochlorite, while potassium persulfate appears to carry out the oxidation rather slowly by some indirect process.

Attention was called earlier to the fact that in the presence of NH_4OH the sodium hypochlorite behaved in a peculiar manner, both in the case of manganese and of nickel. In the case of nickel it will be recalled that while sodium hypochlorite oxidizes nickelous hydroxide readily to the dioxide in the absence of NH_4OH, it does not do so in the presence of this reagent. In the case of manganese, when the solution of Mn^{++}, NH_4Cl, and NH_4OH was treated with sodium hypochlorite, oxidation of the Mn^{++} with precipitation of $Mn(OH)_3$ and MnO_2 started somewhat slowly and then proceeded fairly rapidly, but in a short time the precipitate began to go back into solution again. The first time this was encountered the slight purple tinge to the solution led to the guess that the manganese precipitate was being oxidized further to permanganate ion, but the depth of color was not sufficient to correspond to the amount of manganese present. Also it seemed wholly unlikely that manganese could be oxidized to a permanganate in a strongly ammoniacal solution. Finally, the addition of NaOH to the solution caused a reprecipitation of the manganese which was much more rapid than could be accounted for by the possible reduction of a permanganate by ammonium hydroxide. This led to a recognition of the fact that in the redissolving of the manganese dioxide the manganese was being converted again to Mn^{++}.

Such an actual reversal of a reaction is seldom encountered except as local reactions while reagents are being mixed (or occasionally on students' papers). The explanation was found in the fact that sodium hypochlorite will oxidize ammonia to hydrazine, which is a powerful reducing agent. The rate of oxidation of Mn^{++} by the hypochlorite is greater than that of oxidation of the ammonia so that for a time the amount of the precipitate increased; however, with excess of the hypochlorite present the oxidation of the ammonia continued after the manganese had largely been precipitated, and when the concentration of hydrazine had been built up sufficiently, the manganese dioxide began to be reduced faster than it was being formed and so it went back into solution again as Mn^{++}. The purple is probably due to a colloidal suspension of $Mn(OH)_3$ produced by the competition of the two reactions.

On realizing that ammonia is thus easily oxidized to hydrazine, it seemed worth while to try certain additional experiments involving this reducing agent. To test its efficiency in reducing MnO_2, a suspension of the latter was set up by adding about 1 ml. of H_2O_2 to a solution containing 10 mg. of Mn^{++}, 5 ml. of NH_4Cl, and 10 ml. of NH_4OH. The excess of H_2O_2 was promptly removed by decomposition under the influence of the precipitate. When about 0.5 g. of hydrazine hydrochloride was added to this system with swirling, the precipitate dissolved quickly.

Next, to see how rapidly the hypochlorite oxidizes ammonia to hydrazine and to demonstrate the reducing action of this mixture on NiO_2, the tube was used in which $Ni(OH)_2$ had been oxidized by NaClO in the absence of NH_4OH. To this tube was added 5 to 10 ml. of the reagent NH_4OH and the mixture shaken. An obvious lightening in color occurred promptly, leaving a dark green precipitate. On further shaking this precipitate became much lighter in color. A further test on NiO_2 was applied by using a tube in which NiO_2 had been precipitated by $K_2S_2O_8$ in the presence of NH_4OH. On adding 5 to 10 ml. of NaClO to this tube and mixing, this precipitate also changed to a gray green as the NiO_2 was reduced by the hydrazine formed through the reaction of NaClO on the NH_3.

A third test of the reducing power of hydrazine was carried out on a solution of cobaltic ammonia ion. Two duplicate solutions were set up, each using 10 mg. of Co^{++}, 5 ml. of 5 *N* NH_4Cl, and 10 ml. of 5 *N* NH_4OH; then 1 ml. of H_2O_2 was added to each to oxidize the cobalt to the cobaltic ammonia form. Next, about 0.5 g. of hydrazine hydrochloride was added to one of the tubes, keeping the other for comparison. No immediate change in color took place, indicating that hydrazine is not a good reducing agent for cobaltic ammonia ion. And yet the oxidation potential of cobaltic ammonia ion is intermediate between that of NiO_2 and $Mn(OH)_3$, both of which are readily reduced by this reagent.

In view of the slowness of reduction of cobaltic ammonia ion by hydrazine, it seemed interesting to reverse this last experiment and try oxidizing cobaltous ammonia ion in the presence of hydrazine. Would the hydrazine prevent the oxidation of the cobalt, or would it be oxidized first, corresponding to the very low value of the oxidation potential of the N_2/N_2H_4 system?

Three solutions were set up, each containing 10 mg. of Co, 5 ml. of 5 *N* NH_4Cl, and 10 ml. of 5 *N* NH_4OH. To each was added 0.5 g. of hydrazine chloride and the solution swirled until the salt was dissolved. Five ml. of H_2O_2 was then added to the first solution. A moderately deep red color developed immediately, not visibly different from that obtained in the absence of the hydrazine. Evidently the oxidation of the cobaltous ammonia ion proceeded normally without interference from the hydrazine. To the second tube was added some potassium persulfate. In this case the color developed slowly without the formation of the greenish blue color observed in the absence of the hydrazine. Evidently the hydrazine keeps this odd form of cobalt reduced but permits the direct oxidation to cobaltic ammonia ion to proceed. Interestingly enough,

under these conditions it takes much longer to complete the oxidation to the cobaltic ammonia form than when the indirect mechanism is permitted. The third tube was treated with sodium hypochlorite. Immediately a marked effervescence occurred with only a slight deepening in color of the solution. In this case the hydrazine is being oxidized to nitrogen more readily than the cobaltous to the cobaltic ammonia form. Only in this last case, therefore, does the reaction proceed in the manner in which one might expect from the various oxidation potentials involved.

An over-all comparison of the experiments that have been described shows that in considering the ability of oxidizing agents to carry out oxidations and of reducing agents to carry out reductions, it is necessary to deal with specific pairs of reagents. Thus hydrogen peroxide will oxidize Mn^{++} in an ammoniacal solution at pH 9 much more readily than will sodium hypochlorite or potassium persulfate, but hydrogen peroxide will not oxidize $Ni(OH)_2$ appreciably to NiO_2 although both of the other reagents carry out this reaction readily. In the presence of ammonium hydroxide potassium persulfate is the only one of the three which oxidizes $Ni(OH)_2$ to NiO_2. Again, hydrogen peroxide oxidizes cobaltous ammonia ion much more rapidly than does sodium hypochlorite or potassium persulfate, and yet sodium hypochlorite is the only one of the three which readily oxidizes NH_3 to N_2H_4 or N_2H_4 to N_2. Similarly, hydrazine will readily reduce MnO_2 or NiO_2 in an ammoniacal solution but not $Co(NH_3)_6^{+++}$. On examining these results in the light of the oxidation potentials for the various reagents, it will be observed that in all cases where oxidation-reduction reactions occur the corresponding oxidation potentials are favorable; but in many cases where the oxidation potentials appear to be favorable, no reaction takes place or the reaction is relatively slow. The most extreme case of this latter type is found in the relative inertness of the potassium persulfate hydrazine solution where the normal oxidation potentials of the two reagents are $+2.05$ and -0.85, respectively.

Since these reactions were first encountered in connection with the practical problem of trying to devise an improved method for the qualitative separation of manganese, nickel, cobalt, and zinc, it will not be out of place to note some of the differences observed in the actual use of these reagents.

For the precipitation of manganese by oxidation in the ammoniacal solution, hydrogen peroxide worked rapidly and effectively in the cold; potassium persulfate required the application of heat and then gave effective precipitation; but with sodium hypochlorite, after warming the solution and letting stand two or three minutes before filtering, the precipitation was definitely incomplete. In this last case, with 50 mg. of manganese about 95 per cent was precipitated, but with 5 mg. not over 10 per cent was precipitated by this procedure. On this basis it would appear that hydrogen peroxide was the best reagent for this reaction, potassium persulfate next best, and sodium hypochlorite poorest; however, when the precipitation was carried out in the presence of 50 mg. of cobalt, it was found that the precipitate obtained by oxidation with sodium hypochlorite carried down a negligible amount of cobalt, the one from hydrogen peroxide carried a small amount of cobalt, and the one from potassium persulfate carried what was roughly estimated as 20 to 30 per cent of the original amount of cobalt.

In the next step, in which excess of NaOH was added to the cool filtrate from the manganese precipitate, a black precipitate of NiO_2 was obtained when potassium persulfate had been used, a green to brown precipitate when sodium hypochlorite had been used, and a green precipitate or no precipitate following oxidation by hydrogen peroxide. In the case of sodium hypochlorite the nickel precipitated as nickelous hydroxide and any manganese not previously precipitated came down with the nickel. Even in the absence of nickel the rest of the manganese was fully precipitated at this point. In the case of hydrogen peroxide, if manganese was present, the excess of hydrogen peroxide was decomposed and the nickel then precipitated in the regular manner as $Ni(OH)_2$; however, in the absence of manganese the hydrogen peroxide kept the nickel from precipitating until after the excess had undergone decomposition. On examining the three precipitates by dissolving in HNO_3 and H_2O_2 and testing the solutions, the precipitate obtained after use of sodium hypochlorite was found to contain a small amount of manganese and a very small amount of cobalt. The precipitate obtained after use of hydrogen peroxide contained no manganese but did give a fair test for cobalt. The precipitate obtained after use of potassium persulfate also gave no test for manganese, but it gave a strong test for cobalt. As a matter of fact, when 50 mg. each of cobalt and nickel were used in the experiment, the final solution of nickel nitrate contained sufficient cobalt to give it a distinctly pink tinge. Thus potassium persulfate gave the poorest separations of cobalt from both manganese and nickel; sodium hypochlorite gave a poor separation of manganese from nickel and a good separation of cobalt from both manganese and nickel; and hydrogen peroxide gave a good separation of manganese from nickel, a fairly good separation of manganese from cobalt, and a fairly good separation of nickel from cobalt only if manganese had been present. On this basis it appeared that sodium hypochlorite was the best of the three for these separations, since the major supplementary procedures involved with this reagent were only (1) testing the nickel nitrate solution for manganese, and (2) avoiding interference of manganese with the test for nickel by applying the latter in an acetic acid solution or after filtering out the MnO_2 in an ammoniacal solution.

In connection with the poor separation of cobalt from manganese and nickel when potassium persulfate was used as the oxidizing agent, two points may be noted. First, in the oxidation of cobaltous ammonia ion by potassium persulfate the curious color noted suggests the possibility of a colloidal solution of $Co(OH)_3$ or

the verge of precipitation. If this were the case, the formation of the precipitate of MnO_2 might carry down an appreciable amount of this material. Second, in the precipitation of NiO_2 by adding excess of NaOH to the cool solution, the actual concentration of OH^- set up is approximately 0.4 *M*. Calculations based on the solubility product of $Co(OH)_3$ (2.5×10^{-43}) and the ionization constant of $Co(NH_3)_6^{++}$ (2.2×10^{-34}) show that the solution should be more than saturated with respect to $Co(OH)_3$ and that at equilibrium most of the cobalt should precipitate even in the cold. The fact that a considerable fraction does precipitate with NiO_2 but not with $Ni(OH)_2$ suggests a difference in surface chemistry of the two precipitates whereby $Co(OH)_3$ may be carried down by one but not by the other. Incidentally, the fact that the solution of cobaltic ammonia ion is actually more than saturated with respect to cobaltic hydroxide may be shown by preparing such a solution, adding excess of NaOH, and then letting stand in a well-stoppered bottle. After about a day a small precipitate of $Co(OH)_3$ can be seen, and this gradually increases in amount over a period of several weeks.

The curious action of hydrogen peroxide in preventing precipitation of the nickel when NaOH is added to a solution of nickel ammonia nitrate can only be accounted for as a sort of "dog in the manger" effect. In terms of the concentrations of Ni^{++} and OH^- a precipitate of $Ni(OH)_2$ should form. The green color of the solution suggests that the $Ni(OH)_2$ is present in colloidal solution, with the hydrogen peroxide somehow preventing the aggregating of these particles to form a precipitate. This may be an oxidation effect without the reaction penetrating deeply enough to affect the color seriously. The catalytic decomposition of the hydrogen peroxide, which then follows at a moderate rate, probably involves an alternate oxidation and reduction by the hydrogen peroxide at the surface of the colloidal particles of $Ni(OH)_2$. It is to be noted that this decomposition does take place more rapidly in this case than when the $Ni(OH)_2$ is precipitated in the absence of the ammonium hydroxide. Also, when precipitation actually starts after part of the hydrogen peroxide has been decomposed, the solution is a fairly dark green in color and the precipitate is also fairly dark, changing to lighter green some time later.

SUMMARY

Attention has been called to several cases in which there is little connection between the strength of sodium hypochlorite, hydrogen peroxide, and potassium persulfate and the readiness with which they carry out particular oxidations; or between the strength of Mn^{++}, $Co(NH_3)_6^{++}$, $Ni(OH)_2$, NH_3, and N_2H_4 as reducing agents and the readiness with which they carry out specific reductions.

1. Sodium hypochlorite is the only one of the three oxidizing agents which oxidizes ammonia readily in an ammonium chloride, ammonium hydroxide solution. Curiously enough, the first product of this oxidation is hydrazine, a much stronger reducing agent than the ammonia itself.

2. Hydrogen peroxide acts much more rapidly than either of the others in oxidizing Mn^{++} to $Mn(OH)_3$ or $Co(NH_3)_6^{++}$ to $Co(NH_3)_6^{+++}$, but it fails to oxidize $Ni(OH)_2$ to NiO_2, and, in sufficient excess, even prevents the precipitation of $Ni(OH)_2$ when excess NaOH is added to a solution of nickel ammonia nitrate.

3. Potassium persulfate is the only one of the three which oxidizes $Ni(OH)_2$ to NiO_2 in the presence of NH_4OH. The formation of hydrazine by the sodium hypochlorite accounts for the lack of oxidation of the $Ni(OH)_2$ by this reagent, but it is not at all clear why the oxidation does not take place with hydrogen peroxide. In fact, one of the most curious anomalies noted is that hydrogen peroxide will oxidize $Mn(OH)_3$ to MnO_2 in an ammoniacal solution and yet will reduce NiO_2 to $Ni(OH)_2$ in such a solution. The oxidation potentials involved are approximately 0.8 volt for the $MnO_2/Mn(OH)_3$ system and 0.5 volt for the $NiO_2/Ni(OH)_2$ system.

4. Hydrazine quickly reduces $Mn(OH)_3$ to Mn^{++}, NiO_2 to $Ni(OH)_2$, and ClO^- to Cl^- in an ammoniacal solution, but fails to react readily with $Co(NH_3)_6^{+++}$, H_2O_2, or $K_2S_2O_8$.

There has been much talk that in the future much of the work that has been done in educational institutions will be taken over by institutes devoted exclusively to research. Doubtless there will be an increase in the number of such laboratories and doubtless also they will make noteworthy contributions to knowledge. I have a strong feeling, however, that the great bulk of the contributions will continue to come from educational institutions where research and teaching are combined.

We must continue to look to the universities and colleges for our supply of trained men—no other institutions are equipped for this task. There is a great stimulus to both teaching and research to have the two combined. Any purely research organization has a great tendency to become narrowly specialized since it lacks the necessity of reviewing its work continuously from the standpoint of imparting its results to other than already trained specialists.

The maintenance of our graduate schools at a high level of efficiency is therefore a matter of the utmost importance if we as a nation are to maintain leadership in science and derive maximum benefit from what may be in science.—Frank B. Jewett, President, National Academy of Sciences.

Report of the
NEW ENGLAND ASSOCIATION of CHEMISTRY TEACHERS

A Brief Review of Plastics Chemistry[1]

ROBERT P. COURTNEY

Bakelite Corporation, Bloomfield, New Jersey

OUR knowledge and understanding of the chemistry of plastics have not provided us with the sort of precise formal system which one likes to present to first-year students in a scientific subject—a system with a definite symmetrical pattern, every bit of information falling into its own indisputable place, and every place in the pattern filled with its own bit of information. In all truth most of our formal systems of chemistry idealize the facts, if I may put it that way.

Historically, few of those things which we call plastics involve newly discovered basic reactions. When we first poked our sooty faces out of the mysterious magic cave of the alchemist and decided to be chemists, we became purists almost overnight. We acquired a faith that all things are governed by immutable laws, and we set out diligently, using our newly appreciated experimental method, to wrest from nature the knowledge which would enable us to formulate those laws and understand them. That was good, but through this attitude we developed the slavishness to the exact formal presentation.

Many of the organic chemical complexes which form the base materials of what we call "plastics" were discarded by the early chemist because they did not seem fitted for experiments designed to develop the fundamental laws which he was trying to formulate.

No doubt all of us have at one time and another searched quite far back into the early chemical literature. We may have noticed many items like the following purely imaginary example. The researcher put 100 grams of substance A and 50 grams of substance B into a reaction vessel and allowed them to react under controlled temperature and pressure for a definite time. He then analyzed the resultant mass by careful fractional distillation and re-crystallization and found that he had, say, 10 grams of unreacted A, five grams of unreacted B, 75 grams of a new material of rhombic crystalline form melting at 75°C. and boiling at 121°C. with molecular weight 49. He carried out an elementary analysis, established an empirical formula, and prepared and identified derivatives until he could establish the structure of the molecule. He announced that this new chemical had been prepared by this procedure to give 50 per cent of a theoretical yield.

But what became of the remaining 60 grams of the original reactants? Again and again we find that it was a tarry or pitch-like residue of uncertain character. Undoubtedly it eventually reached the stone crock on the floor at the end of the laboratory bench.

It was of little interest to these early chemists because it was too complex to lend itself to the methods available for study and so did not appear to be useful in determining basic laws of chemical behavior. It represented only the loss which prevented a 100 per cent yield.

Our slightly better methods of today still give us indisputable knowledge of the structure of few, if any, of these tarry, resinous, rubbery masses. Phenol-formaldehyde plastics are among the earliest synthetic plastics known. Volumes of literature have been written about researches on them. We believe we know a little about the primary reactions, but only a little. When we consider the infusible insoluble stage, many, if not all, of our ideas as to reaction and structure are highly speculative, to say the least.

Late in the 19th century and early in this one some chemists, outstanding among whom was the late Dr. Leo H. Baekeland, began to realize that since chemistry is the science of matter and since these previously scorned substances are unquestionably matter, perhaps they warranted the courtesy of the chemist's attention. For years cellulose nitrate and phenol-formaldehyde products were the only synthetic plastics known outside the laboratory. Then came urea-formaldehyde, a willful child who was difficult to tame, cellulose acetate, polystyrene, the vinyls, acrylates, synthetic rubbers, and now we can almost expect the announcement of a new one in every monthly journal. The tarry residue has come into its own.

Now to proceed to the general discussion of plastics chemistry. All of the high polymers to which we shall refer in this connection are bound together by homopolar covalent bonds, which means that the bond, if single, displays dissociation energies of 40,000 to 100,000 cal. per mol. The polymers appear to have from several hundred to several thousand monomer units per

[1] Based on an address delivered at the Sixth Summer Conference of the N.E.A.C.T., Connecticut College, August 28, 1944.

molecule. We shall refer only to organic high polymers, consisting primarily of C, H, O, and N with sometimes Cl or S. The units of these large polymers are usually referred to as macromolecules.

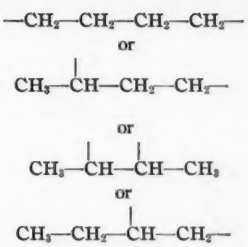
We may roughly divide the field into (*a*) polycondensation reactions and (*b*) polymerization reactions. I say roughly, because we shall see that, as usual, there is considerable overlapping.

In the first class we have those reactions in which two similar or dissimilar initial molecules unite, splitting off water, and these in turn with others in a similar way. These are all step reactions—that is, each individual union of one molecule with the next is similar to each other union, the initial reaction neither increasing nor decreasing the tendency to react with another unit. Except for an acceleration due to initial evolution of heat, these reactions proceed at a rather uniform rate. In this class we include phenol-formaldehyde, urea formaldehyde, and alkyd resins. But let us note here that after the initial condensation, it appears that a further polymerization takes place without splitting off water, leading to the final, insoluble, infusible stages so that, as we stated, our classification is a rough one.

We include in the second class those, usually permanently thermoplastic, products which result from the reaction of similar or dissimilar molecules without loss of water. These reacting molecules are always unsaturated or unstable. The reactions follow the course of what we refer to as a chain reaction and, we believe, lead largely to chain molecules—that is, long, almost uni-dimensional, molecules. In these reactions it appears that the molecules do not necessarily react simply because, in the course of their kinetic movement, they happen to collide. It seems that at the time of collision they must also be in a suitably "excited" state. At any rate, these chain reactions do not start of themselves as rapidly as would be expected from the calculated number of collisions. But whether the reaction of the first molecular pair be initiated by a catalyst, a light quantum, or what, an induction period is required before the reaction really gets under way. After that, the reacted pair seems to have the ability to react very readily with another and then another molecule, building up a long chain of monomer units bound together by primary valence bonds. Many properties of these products lead us to the belief that such long-chain molecules really exist. During this propagation period the reaction proceeds very rapidly. Eventually it slows up and stops like any well-behaved reaction, but what makes it stop is not so clear.

Let's take our simplest example. It's our simplest example in so far as the fundamental building block is concerned, but by no means simple from the point of view of engineering nor of understanding its properties.

Ethylene, $CH_2{=}CH_2$, is the simplest of the olefins. Place it under suitable conditions for reaction and during an induction period, by action of light quanta, catalyst, or some such agent, a number of molecules eventually collide in pairs and in an "excited" state and react to give

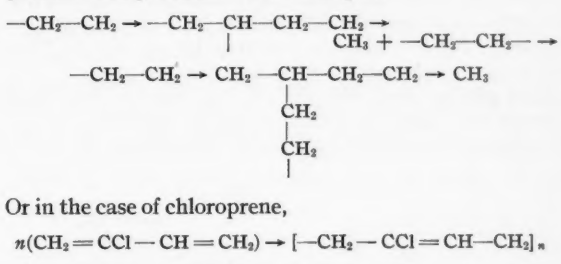


Certain considerations make us believe that hydrogen migrates rather freely in the course of these reactions, but in each case we have a larger unit which is also "excited" due to its free valence bonds and in its turn reacts very readily with the next molecule with which it collides, giving a still longer molecule still "excited" and ready to react again, and so on like the old story you will remember, "Then another locust came and got another grain of corn."

But what stops the reaction? It is not necessarily stopped by exhaustion of the initial monomer because in many cases unreacted monomer must be removed at the end in commercial processes in order to have a useful product. Staudinger at one time held to the opinion that the extreme chain lengths lead to the effect of the free valence becoming negligible. I believe he later abandoned this view. At any rate it is not compatible with the fact that the molecules of a specimen of high polymer are not all of the same length, some being relatively short. Some termination is doubtless due to large ring closure, but the evidence seems to be that there is less of this than one might think. Reaction with impurities might account for saturated end groups in some cases. I think, though, that the honest answer is that we don't know how these reactions terminate. Perhaps the king just gets tired of hearing that "another locust came and got another grain of corn" and decides to call it a day.

It should be pertinent now to consider what sort of structures we believe to be built up in these high polymers, how big the molecules are, and what their shape may be.

So far, in considering the polymerization of unsaturated compounds we have thought in terms of straight unbranched chains. It is doubtful if this result is ever achieved in the case of every macromolecule in a given sample. Even in the simple case of ethylene, which we considered before, branching of the chain is not only possible but probable. For example,



Or in the case of chloroprene,

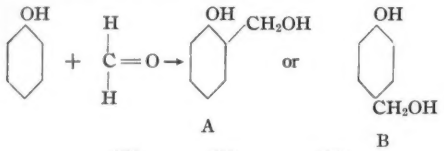
$$n(CH_2{=}CCl{-}CH{=}CH_2) \rightarrow [-CH_2-CCl{=}CH-CH_2]_n$$

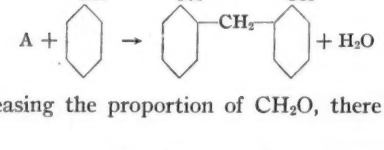
where the second member of the equation represents a

FIGURE 1

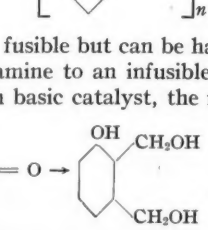
chain which continues for n units. It will be seen that each unit contains a double bond which may open up to "cross link" with another chain, or be cross linked through sulfur by vulcanization. I think we do not know beyond a doubt that "cross linking" is what occurs. Such a theory seems to fit the data. What we do know is that in those cases where "cross linking" or branching is theoretically possible, we find the relative ability to swell, dissolve, etc., compatible with our theory.

From this we progress to our polycondensations. Here we find the properties we associate in our minds with "cross-linked" or network structure to a still greater extent. Taking as our example the phenol-formaldehyde reaction, we know fairly well now what some of the initial condensation products are. For example, phenol and formaldehyde with an acid catalyst react to form phenol alcohols.



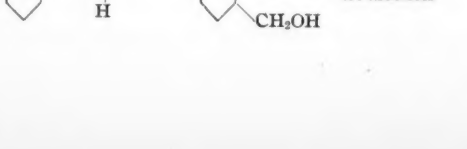


Or increasing the proportion of CH_2O, there is probably:

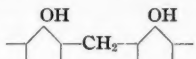


This product is fusible but can be hardened with hexamethylene tetramine to an infusible product.

Whereas with basic catalyst, the reaction is



which substances harden on heating. One of many formulas proposed for the hardened product is:



Frankly we don't know what the final structure is; but whatever time and further work may finally decide the structures of high polymers to be, we know that we have products with different flow characteristics, solubilities, swelling characteristics, etc., which it has been proposed to explain by the idea of (1) straight chain molecules, (2) branched chains, and (3) networks or cross-linked chains, this last reaching the extreme in the infusible, insoluble end products of polycondensations. Even if our conception is accurate, we probably never have a pure case of one of these unadulterated with the others.

Average molecular weights of high polymers are determined by various methods which do not always give agreeing results. There has been much controversy as to whether we are actually measuring molecular weight or something else. The lack of agreement between methods no doubt results to some extent from branching and cross linking. The method proposed by Staudinger for determination of molecular weight by measurement of viscosity in dilute solution has found most widespread use.

Now if we cause one of these monomeric reactants to polymerize under varying conditions of temperature and time, we find that the product will vary over quite a wide range in flow characteristics and average molecular weight. The product of one set of conditions will be more useful for commercial application than that of another. We would like to know what we have in each case. We suspect that all the macromolecules are not of the same molecular weight as the average we have determined.

Therefore means have been devised for fractionation by the ultracentrifuge, fractional precipitation, osmosis, etc. If we so fractionate a given sample of polymer and determine the average molecular weight of each fraction, we may plot the total amount removed at the end of each fractionation against the average molecular weight to get the integral step fractionation curve as shown in *A*, Figure 1. Depending upon the number and smallness of fractions which we have taken, we may smooth out this curve more or less accurately to give *B* in Figure 1. This shows at each point the integral weight of all polymers below the molecular weight indicated. As will be seen by inspection, the slope of this curve expresses at each point the differential weight of polymer of the molecular weight indi-

cated. This slope is graphed in *C* which we call the differential weight distribution curve. If we introduce into our calculations what Stuadinger called the "basal mol," *i. e.*, the molecular weight of a mol of monomer, we get the differential number distribution curve *D*, which indicates the number of molecules at each molecular weight.

The differential weight distribution curve *C* is the one most commonly used because it tells us at a glance what proportion of our starting material has been converted to high, medium, and low polymer. We know that by so selecting our reaction conditions as to move the maximum of this curve to the right, we decrease the flow of our product, increase its softening point, and reduce its rate of solubility. If we cause the peak to move to the left, we change thsse properties in the opposite sense.

There are a great many high polymeric materials useful as commercial plastics beyond those few I have used as examples. I could have taken time from this brief outline to run through a discussion of a greater number of them and to speculate as to the course of the reactions. In the light of present knowledge, however, they appear so similar in principle that it was thought more profitable to cover the ground that we have, even at the expense of being superficial.

SUMMER CONFERENCE

The eighth annual Summer Conference of the N.E.A.C.T. merits serious consideration by all chemistry teachers who wish to keep abreast of developments in chemistry fostered by the recent war. The Conference will be held August 19 to 24 at Middlebury College, Middlebury, Vermont, and it is open to all N.E.A.C.T. members. Nonmembers can attend by joining the association.

From the research laboratories of the General Electric Company Dr. Francis J. Norton will give an illustrated lecture on "Silicones," Mr. Sidney Roberts of the Aetna Life Insurance Company Medical Laboratory will lecture on "Chemistry in Life Insurance," and Dr. Andrew J. Scarlett of Dartmouth will present "A G. I. Chemist in a G. I. School in France." These are typical program numbers.

Dr. William B. Meldrum of Haverford College will have charge of a symposium on "Electrolysis" that will include Dr. John A. Timm of Simmons College and Professor Frank T. Gucker of Northwestern University in the panel. All speakers are well-known authors. A symposium on "Colloids" is being organized by Dr. Ernst Hauser of the Massachusetts Institute of Technology.

Full details of the program and arrangements for housing and meals at the college can be made by writing to the Conference Registrar and Treasurer, Miss Helen Crawley, Walnut Hill School, Natick, Massachusetts. As in the past, the N.E.A.C.T. Summer Conference will feature professional advancement, friendly discussions, and low costs in a vacation atmosphere.

LETTERS

To the Editor:

In connection with Dr. Kendall's article on barbituric acid in the January issue of JOURNAL OF CHEMICAL EDUCATION, you will perhaps be interested in knowing that Willstätter, von Baeyer's successor to the chair of chemistry at Munich, used to tell his classes that Baeyer named the acid in honor of a young lady called Barbara whom he adored at that time. Willstätter did not expect us to take that tale seriously; I for one have the same feeling about Dr. Kendall's story. I think Fieser's account is much more probable and in keeping with the mental attitude of the scientists of the 19th century.

F. FROMM

COLLEGE OF THE SACRED HEART
SANTURCE, PUERTO RICO

To the Editor:

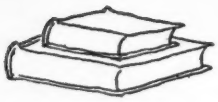
An article entitled "Collection of Spilled Mercury" by Albert F. McGuinn, S.J., published in your September, 1945, issue has just come to my attention. Although I have never collected mercury by the method proposed in the above article, I have had considerable success with an improvisation of my own which is applicable to laboratories, plants, or, in fact, any place where a moderate vacuum is available. The necessary equipment consists of a bottle, a stopper penetrated by two short pieces of glass tubing, two pieces of rubber tubing, and an eye dropper.

In operation the stoppered bottle is connected through one piece of rubber tubing to the source of vacuum while the other piece of vacuum tubing is attached to the bottle at one end and to the eye dropper at the other end. The bottle should be situated at some point not too far above the level of the spilled mercury.

By moving the eye dropper from one pool to another, the mercury can be quickly and conveniently sucked into the bottle. By substituting a capillary tube for the eye dropper, every trace of mercury can be removed from otherwise inaccessible places such as cracks in the floorboards.

WILLIAM R. BURKE

WOODBURY, NEW JERSEY



RECENT BOOKS

THE ELECTRON MICROSCOPE. *E. F. Burton*, University of Toronto, and *W. H. Kohl*, Formerly Chief Engineer, Rogers Electronic Tubes, Ltd., Toronto, Canada. 2nd edition. Reinhold Publishing Corporation, New York, 1946. 325 pp. 125 figs. 16 × 23.5 cm. $4.00.

This volume concerns itself chiefly with the optics of the electron microscope. Its first 140 pages carry a beautifully logical and elementary explanation of the dual theory of light and of the behavior of electrons in electric and magnetic fields. For teachers and young scientists these pages should be required reading.

The next 100 pages are the hardest. The section on electron optics is expanded to include electron lenses and is considerably more advanced in treatment than the first part of the book. The subsequent chapters on electrostatic, electromagnetic, and the 1944 Toronto model electron microscope are too specialized and go into too much detail for the beginner. Finally, about 40 pages describe in matter-of-fact style the use and practical applications of the electron microscope.

Authors and publisher deserve great praise for the profusion of drawings and magnificiently reproduced electron micrographs. Replica and shadowing techniques are well illustrated. For these and for their excellent treatment of elementary optics the authors have rendered great service in the educational field.

But a manuscript written in December, 1944, in a field so rapidly expanding as that of the electron microscope can hardly be expected to be up to date in 1946. The authors themselves confess to have written this second edition "handicapped by the unusual load of pressing war work" and "at the suggestion of the publishers." Why, then, was not the appearance of this volume delayed for a few months to give time to include the revolutionary advances of 1945, such as the shadowing technique of Wyckoff and Williams, to bring the comprehensive bibliography up to date, to change the lower limit of the electron microscope from 10^{-6} cm. (1944 value), as shown in the front plate, to 10^{-7} as has now been accomplished?

For the teacher's personal collection this volume is an excellent companion piece to Hawley's "Seeing the Invisible" (THIS JOURNAL, **22**, 312 (1945)—the former for its electron optics, the latter for delineating the field of research for the electron microscope.

HUBERT N. ALYEA

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

SYNTHETISCHE METHODEN DER ORGANISCHEN CHEMIE, Repertorium I. *W. Theilheimer*. S. Karger, Basel and New York, 1946. viii + 224 pp. 16 × 23 cm.

The author and publisher propose a new series of biannual and eventually annual volumes that will provide synthetic methods for the preparation and study of numerous organic compounds. Repertorium I of this series covers rather completely and extensively the chemical literature for the years of 1942 to 1944 inclusive. It is proposed that the forthcoming Volume II will cover the period of 1945 to 1946, and will also include such reactions of the 1942–44 period as were not available, because of war conditions, when the first volume was being prepared. Subsequent volumes thereafter are to be prepared and published annually.

Brief directions are given for the preparation of 793 different organic compounds. Each entry is accompanied by one or more references to recent chemical literature. No claim is made for complete citations of the literature involved during the years of 1942 to 1944, but references and directions were chosen from all similar reactions available because of the excellence of yields produced or ease of manipulation. All journal abbreviations are the same as those employed in Beilstein's "Handbuch der Organischen Chemie." Cross references are made where any compound or reaction involved might logically be included under more than one classification.

The general plan of the book is distinctly different from anything else available. The chief emphasis is placed upon the types of reaction involved. The organic compounds used to illustrate each are then listed under the type reactions. Seven major types of reactions are used for the purpose of classification—namely, loss of groups or atoms with 19 sub-headings, addition, exchange, electrolytic transformation, ring closure, ring opening, and rearrangement with 26, 49, 0, 0, 0, and 9 subclassifications, respectively.

The entire plan of the book, its system of classification, the adequacies and limitations of each reaction are discussed in the Geleitwort, Vorwort, Systematik, and Alphabetisches Register. The index is unusually complete and specific and includes suggested synthetic methods of preparation, name-reactions, chemical reagents, reactants and resultants in chemical transformations. Also a table of abbreviations that are used is included.

It is not often that a volume or series of volumes of such unique potentialities makes its appearance. This first volume is in no sense a duplication or competitor of existing present compilations such as "Organic Syntheses," "Beilstein's Handbuch der Organischen Chemie," "Houben's die Methoden der Organischen Chemie," or "Chemisches Zentralblatt." The methods of assembling the data, its system of classification, the points of emphasis, and text contents, while resembling each in some respects, are also distinctly different from the existing literature. This volume places chief emphasis upon the types of reactions and uses each of the 793 organic preparations as examples to illustrate the basic principles involved. However, directions of preparation, yields, and experimental conditions are usually complete enough to enable the average laboratory worker to follow them without further aid. The references to the literature which accompany each entry will quickly provide additional details when necessary.

It would be hard to find a greater assemblage of useful information, with emphasis upon type reactions and methods of preparation, than is present in these 224 pages. Every alert research worker in the organic field should have ready access to these volumes of which this is the first. Many of the preparations could be used to advantage in the school organic laboratory where emphasis is placed upon preparations as a means of teaching techniques and principles. We can only hope that labor, paper, and printing conditions abroad will provide for a generous and wide-spread distribution of this valuable volume in this country.

RALPH E. DUNBAR

NORTH DAKOTA AGRICULTURAL COLLEGE
FARGO, NORTH DAKOTA

ESSENTIALS OF GENERAL CHEMISTRY. *B. Smith Hopkins*, Professor of Inorganic Chemistry, Emeritus, and *John C. Bailar, Jr.*, Professor of Chemistry, University of Illinois. D. C. Heath Company, Boston, 1946. v + 520 pp. 216 figs. 45 tables. 15 × 22.5 cm. $3.50.

The author and publishers are to be congratulated for the appearance of this book. The cover is dark blue, the title is set in gold and bordered with Florence flasks arranged in rows and lying top to bottom. The paper is good and of the compact form so as to get the 520 pages in a thickness of about 2.5 cm. It has an appeal to the eye that the reviewer has not seen in a text for a long time.

The location of important tables has been well chosen. The electromotive series of the common metals is on the flyleaf, and periodic charts are on the last page and the inside of the back cover. Both the usual Mendeleeff table and the extended form are given. Page 2 of the text has a map of North America showing the sources of raw materials for the chemical industry. In fact, the authors have attempted all through the book to arouse the interest of the student by giving greater emphasis to industrial applications and sources of materials. Another teaching device used is the placing at the end of each chapter a list of new

terms introduced in the chapter. A set of exercises and reference for further reading is also included with each chapter.

History is practically excluded. There is a very brief statement under oxygen on Scheele, Priestley and Lavoisier and several other references to the men connected with various projects, but many old friends such as Cavendish Moseley, Lewis, Langmuir, Madame Curie, etc., are missing. Likewise there are no pictures of the scientists that grace the usual text.

The order of the material is approximately the conventional form. The structure of matter, electrovalence, and covalence is discussed in Chapter 3. The coordinate bond is reserved for the ammonia chapter. All through the book continuous use is made of the dot (·) and cross (x) system of showing the valence electrons in compounds. This is an excellent feature since it serves to show the source of the electrons in most of the common compounds. The radium disintegration series and artificial radioactivity are entirely omitted. A short paragraph on radium is placed with the alkali earth elements. Atomic fission is mentioned under uranium. The metallic elements are discussed in the order of the Periodic System.

Organic compounds are assigned two chapters, and these include a sufficient treatment on newer products as synthetic rubber and medicinal agents to arouse interest. The authors are to be complimented on naming the peroxy acids of sulfur in accordance with the recommendations of the International Committee. It is regretted that many of the complex compounds are not named.

This is definitely not an encyclopedia, and one desiring detailed information on many topics must seek elsewhere. The reviewer gains the impression that the authors have included only the material that they believe can be assimilated in a first-year course.

The book is well written and in a manner that should appeal to the student. It is easy reading, the explanations are clear and to the point.

CHARLES E. WHITE

UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

ORGANIC REAGENTS FOR ORGANIC ANALYSIS. By the Staff of Hopkin and Williams, Research Laboratory, London. Chemical Publishing Company, Inc., Brooklyn, 1946. 175 pp. 13 × 21.5 cm. $3.75.

Hopkins and Williams, Limited, is a London company making organic and inorganic laboratory chemicals. In the course of their work the staff has collected together recent data on the use of organic reagents for the preparation of derivatives, has checked published melting points, and determined new ones. The present volume summarizes the data collected by W. C. Johnson, chief chemist, and his colleagues, R. J. Shennan and R. A. Reed.

The first 32 pages are devoted to a discussion of selected reagents for preparing derivatives of 18 classes of organic compounds. Each discussion is brief but to the point. In the second part of the book (pp. 33–106) 42 selected reagents are briefly discussed. Practical and pertinent comments concerning the reagents are given with references to the literature.

The third portion of this book (pp. 109–166) consists of tables of 20 classes of compounds which are arranged alphabetically under each class, and the melting points of derivatives are given under each reagent. The authors have inserted many new melting points and corrected old ones. Such changes are indicated by the type.

This little volume will be of use to analytical or control laboratories for reference purposes when it is desirable to verify the contents of a bottle labeled with the name of the compound. The alphabetical arrangement of compounds (without any physical constants) renders it of doubtful value for teaching or research. The compounds in the tables are not included in the brief index (pp. 167–175) which concludes the book. The price of $3.75 is entirely too high for this small handbook.

R. L. SHRINER

INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

SOAP IN INDUSTRY. *Georgia Leffingwell*, Editor, "Glycerine Facts and Soap Uses in Industry," and *Milton Lesser*, Technical Editor, "Drug and Cosmetic Industry." Chemical Publishing Company, Brooklyn, 1946. viii + 204 pp. 13.5 × 21.5 cm. $4.00.

According to the authors, "This book is intended as an indicative rather than an exhaustive survey of the industrial uses of soluble soaps, *i. e.*, potash and soda soaps as contrasted with the heavy metal soaps, with particular emphasis on the growing place of these soap uses in our industry." There are 23 chapters with the following headings; Animal Husbandry, Building and Construction, Cosmetics, Dentistry, Inks and Ink-making, Insecticides, Leather, Lubricants, Milk Production, Mining and Ore Treating, Oil Production, Paints, Paper and Packaging, Plastics, Polishes and Cleaners (Metal and Glass), Polishes and Cleaners (Wood), Restaurant Sanitation, Road Building and Maintenance, Rubber Production, Textiles, Textiles (Dyeing and Printing), Wool Production, and Miscellaneous.

Each chapter gives a brief description of the ways in which soaps are used in the various industries; to illustrate these uses, over eighty formulas are given for cleaners, polishers, penetrants, dye mixtures, degreasers, etc.

The information is primarily of value to the industrial chemist; the teacher of colloidal chemistry will find some interesting material which might be used in laboratory experiments. The price seems excessive, particularly in view of the fact that most of the information is available in patents and formularies.

ARTHUR A. VERNON

NORTHEASTERN UNIVERSITY
BOSTON, MASSACHUSETTS

CHEMICAL CRYSTALLOGRAPHY: AN INTRODUCTION TO OPTICAL AND X-RAY METHODS. *C. W. Bunn.* Oxford University Press, New York, 1946. xii + 422 pp. 234 figs., including 13 plates. 15.5 × 24.5 cm. $7.50.

Quoting from the author's preface: "Crystallographic methods are used in chemistry for two main purposes—the identification of solid substances, and the determination of atomic configurations; there are also other applications, most of which, as far as technique is concerned, may be said to lie between the two main subjects. This book is intended to be a guide to these methods. I have tried to explain the elementary principles involved, and to give as much practical information as will enable the reader to start using the methods described. I have not attempted to give a rigorous treatment of the physical principles: the approach is consistently from the chemist's point of view, and physical theory is included only in so far as it is necessary for the general comprehension of the principles and methods described. Nor have I attempted to give an exhaustive account of any subject; the aim throughout has been to lay the foundations, and to give sufficient references (either to larger works or to original papers) to enable the reader to follow up any subject in greater detail if he so desires.

"The treatment of certain subjects is perhaps somewhat unorthodox. Crystal morphology, for instance, is described in terms of the concept of the unit cell (rather than in terms of the axial ratios of the earlier morphologists), and is approached by way of the phenonema of crystal growth. The optical properties of crystals are described solely in terms of the phenomena observed in the polarizing microscope. X-ray diffraction is considered first in connection with powder photographs; it is more usual to start with the interpretation of the diffraction effects of single crystals. These methods of treatment are dictated by the form and scope of the book; they also reflect the course of the writer's own experience in applying crystallographic methods to chemical problems. It is therefore hoped that they may at any rate seem natural to those to whom the book is addressed—students of chemistry who wish to acquire some knowledge of crystal lographic methods, and research workers who wish to make practical use of such methods. If the book should come to the notice of a more philosophical reader, I can only hope that any qualms such as a reader may feel about its avoidance of formal physical

or mathematical treatment may be somewhat offset by the interest of a novel, if rather severely practical, viewpoint.

"The difficulties of three-dimensional thinking have, I hope, been lightened as much as possible by the provision of a large number of diagrams; ..." 234 are included, many of them unusually illuminating. The style is exceptionally readable; printing, paper, and indexes are good.

The book is not a laboratory manual, written around favorite apparatus and techniques—rather, it attempts to impart an understanding of methods and principles, from the simplest to the most advanced. The introductory chapters can be read with profit by underclassmen; the work as a whole goes as far as possible toward explaining why substances of certain composition crystallize as they do with the properties they have as solids. Organic and inorganic chemicals are used extensively as examples rather than the usual preponderance of minerals.

The book is strongly recommended for every chemistry and physics library, for students in its field, and for the numerous chemists who have been impressed, but also somewhat outdistanced, by modern crystallography and who want to grasp its evidences even if they do not practice its techniques.

C. W. MASON

CORNELL UNIVERSITY
ITHACA, NEW YORK

PHYSICAL CHEMISTRY OF CELLS AND TISSUES. *Rudolph Hober*, School of Medicine, University of Pennsylvania, with the Collaboration of *David I. Hitchcock*, School of Medicine, Yale University, *J. B. Bateman*, Mayo Clinic, *David R. Goddard*, University of Rochester, and *Wallace O. Fenn*, School of Medicine, University of Rochester, The Blakiston Company, Philadelphia, 1945. xiv + 676 pp. 70 figs. 58 tables. 15 × 23.5 cm. $9.00.

This is an excellent example of "applied chemistry." It is one of the unfortunate results of our conventional type of laboratory instruction that the student almost inevitably carries away the impression that chemistry is something that takes place in test tubes, beakers, and flasks. In his mind oxygen cannot be disconnected from hard-glass test tubes, acids and bases from burets and litmus paper. In the effort to make first principles *simple* we succeed only in making them *artificial*.

Chemistry can be completely independent of the tools and is not fully appreciated until we study it in its natural setting. It goes on about us, not only in the inorganic world, but more particularly in the organic.

Some years ago there was an oft-quoted statement to the effect that the most important recent advances in chemistry had been in physics, and the most important advances in biology had been in chemistry. It is even more true today, and this book contains the evidence of the latter half of this remark.

According to the preface its subject is physiology, not "physiology from above" but "physiology from below." Physiology is conceived as "a branch of physical chemical science dealing with life as a physical, though exceedingly complex, "system."

This is no mere orientation course in physical chemistry for biologists. One does not get far in its pages before discovering that it requires a good background of chemical training. To the person who has, this will be revealed the application of his, science in this fundamental and important field.

Several authors have contributed sections and one works up progressively through basic physical chemistry and thermodynamics, the properties of large molecules (including a good modern treatment of interatomic and intramolecular forces), cellular surface phenomena, respiration and oxidation, and finally applications to contractility, cell penetration, etc.

The earlier chapters will be found a good introduction to (or review of) general physical chemistry for anyone.

N. W. R.

SCIENCE IN A CHANGING WORLD. *Emmett James Cable*, Head of the Science Department, *Robert Ward Getchell*, Professor of Chemistry, and *William Henry Kadesch*, Professor of Physics, Iowa State Teachers College. Prentice-Hall, Inc., New York, 1946. xviii + 622 pp. 329 figs. 15.5 × 23.5 cm. $5.00.

Here are 320 pages of physics, followed by 125 pages of chemistry, in turn followed by 70 pages of geology, concluding with 82 pages of astronomy. Frequent bold-face paragraph titles, in the best modern textbook style, make for easy, painless reading.

This second (1946) edition brings the first (1940) up to date by substituting the Bohr theory of the atom for the Lewis-Langmuir. Perhaps a third edition will find a way of eliminating the conception of "degree of ionization" of salts.

N. W. R.

BOOKS—WAR VICTIMS

During the war the libraries of half the world were destroyed in the fires of battle and in the fires of hate and fanaticism. Where they were spared physical damage, they were impoverished by isolation. There is an urgent need—now—for the printed materials which are basic to the reconstruction of devastated areas and which can help to remove the intellectual blackout of Europe and the Orient.

There is need for a pooling of resources, for coordinated action, in order that the devastated libraries of the world may be restocked, as far as possible, with needed American publications. The American Book Center for War Devastated Libraries, Inc., has come into being to meet this need. It is a program that is born of the combined interests of library and educational organizations, of government agencies, and of many other official and non-official bodies in the United States.

The American Book Center is collecting and is shipping abroad scholarly books and periodicals which will be useful in research and necessary in the physical, economic, social, and industrial rehabilitation and reconstruction of Europe and the Far East. The Center cannot purchase books and periodicals; it must depend upon gifts from individuals, institutions, and organizations. Each state will be organized to participate in the program through the leadership of a state chairman. Other chairmen will organize interest in the principal subject fields. Cooperation with these leaders or direct individual contributions are welcomed.

What Is Needed: Shipping facilities are precious and demand that all materials be carefully selected. Emphasis is placed upon publications issued during the past decade, upon scholarly books which are important contributions to their fields, upon periodicals of significance (even incomplete volumes), upon fiction and non-fiction of distinction. All subjects—history, the social sciences, music, fine arts, literature, and especially the sciences and technologies—are wanted.

What Is Not Needed: Textbooks, outdated monographs, recreational reading, books for children and young people, light fiction, materials of purely local interest, popular magazines such as *Time*, *Life*, *National Geographic*, etc., popular nonfiction of little enduring significance such as Gunther's "Inside Europe," Halliburton's "Royal Road to Romance," etc. Only carefully selected federal and local documents are needed, and donors are requested to write directly to the Center with regard to specific documents.

How to Ship: All shipments should be sent *prepaid* via the cheapest means of transportation to The American Book Center, c/o The Library of Congress, Washington 25, D. C. Although the Center hopes that donors will assume the costs of transportation of their materials to Washington, when this is not possible reimbursement will be made upon notification by card or letter of the amount due. *The Center cannot accept material which is sent collect.* Reimbursement cannot be made for packing or other charges beyond actual transportation. When possible, periodicals should be tied together by volume. It will be helpful if missing issues are noted on incomplete volumes.